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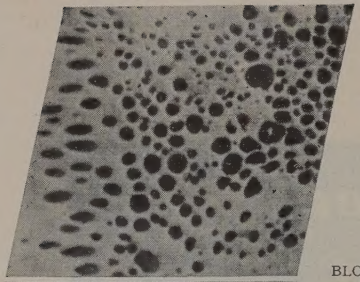

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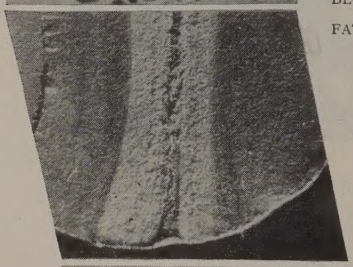

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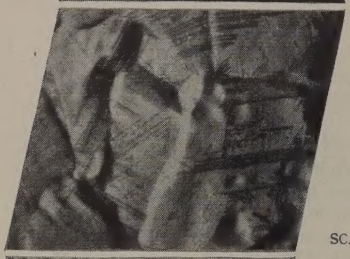

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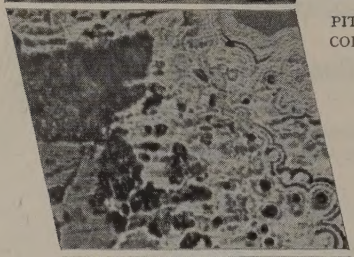

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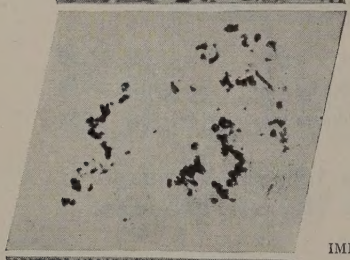

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BEITRAG ZUR ENTWICKLUNG WARMFESTER TITANLEGIERUNGEN

ULRICH ZWICKER

Metall-Laboratorium der Metallgesellschaft A.G., Frankfurt/M. (Deutschland)

(Eingegangen den 1. Januar 1959)

ZUSAMMENFASSUNG

Elektronenmikroskopische Aufnahmen an der Legierung TiAl6 zeigen die Bildung der α_2-Phase bei 500°C. Mit Hilfe von Auslagerungsversuchen wurde die Versprödung an aluminiumhaltigen Legierungen mit über 7% Al untersucht. Durch Zusätze von 3–4% V wird eine Versprödung bei einer Legierung mit 9% Al bei Auslagerung bis 1000 Std. bei 550°C vermieden. Das Verhalten der Legierung TiAl9V3 bei der Herstellung, Verarbeitung, im Dauerstand- und Biegewechselversuch bei Raumtemperatur und erhöhter Temperatur wird beschrieben. Bis zu Gehalten von 0.1% bewirkt Wasserstoff eine Verbesserung des Dauerstandverhaltens gekerbter Proben bei Raumtemperatur.

Wie bei anderen warmfesten Legierungen wird auch bei der Legierung TiAl9V3 eine Art Spannungskorrosion bei Temperaturen über 400°C gefunden. Bei Temperaturen und Belastungsgrenzen, bei denen noch keine durch diese Korrosion verursachte Versprödung auftritt, zeigt die Legierung TiAl9V3 im Vergleich mit den Legierungen TiAl7Mo3, TiAl5Sn2.5 und TiAl6V4 das beste Dauerstandverhalten.

SUMMARY

Electron-microscope photographs of the alloy TiAl6 show the formation of the α_2-phase at 500°C. Aging tests were performed in order to examine the embrittlement of alloys containing more than 7% Al. Addition of 3–4% V prevents the embrittlement of an alloy with 9% Al after aging at 550°C up to 1000 h. The behaviour of the TiAl9V3 alloy during production and working is described as well as that during creep resistance and cyclic bending tests at room and elevated temperature. Hydrogen in amounts not exceeding a content of 0.1% was found to improve the creep resistance of notched samples at room temperature.

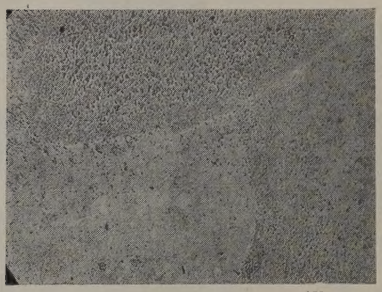
Like other heat-resistant alloys, the TiAl9V3 alloy is susceptible to a kind of stress corrosion at temperatures above 400°C. At temperatures and stress limits at which no embrittlement caused by such corrosion occurs, the TiAl9V3 alloy has a higher creep resistance than either the TiAl7Mo3, the TiAl5Sn2.5 or the TiAl6V4 alloy.

BILDUNG DER α_2-PHASE IN ALUMINIUMHALTIGEN TITANLEGIERUNGEN

Die meisten bisher bekanntgewordenen warmfesten Titanlegierungen enthalten als wichtigstes Zusatzelement Aluminium. Verschiedene Untersuchungen im System Titan–Aluminium haben gezeigt, daß sich bereits bei 6% eine zweite Phase bilden kann[1c,2-4]; die – wie bei Legierungen mit höheren Aluminiumgehalten nachgewiesen wurde – eine geordnete Struktur aufweist[5-7]. Die mechanischen Eigenschaften, insbesondere die Streckgrenze, werden durch die Bildung dieser Phase bei der Auslage-

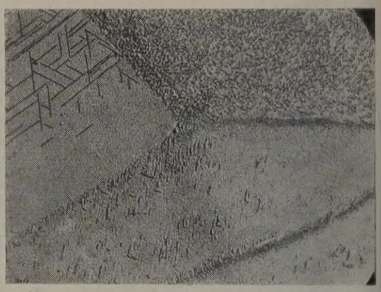
Literatur S. 184

rung verändert[8]. Während bei lichtmikroskopischen Untersuchungen an einer Legierung mit 6% Al die Vergrößerung nicht ausreichte[3], um die einzelnen Teilchen der geordneten Phase aufzulösen, gelang dies jetzt mit Hilfe von elektronenmikroskopischen Aufnahmen*. Das Material wurde aus Reinstaluminium und Titan mit einer Umschmelzhärte von HB 30/10 = 100–110 kg/mm² hergestellt. Die abgeschreckte Probe (Abb. 1) zeigt nur eine geringfügige Aufrauhung des Untergrundes, die möglicherweise dadurch entstanden ist, daß sich bereits Anfänge einer Entmischung ausbilden. Durch eine 100-stündige Auslagerung bei 500°C bildet sich die Überstrukturphase α_2. Die Ausscheidungen erfolgen in Stäbchenform, so daß meist ein Querschnitt (Abb. 2) und weniger häufig ein Längsschnitt (Abb. 3) durch die ausgeschie-



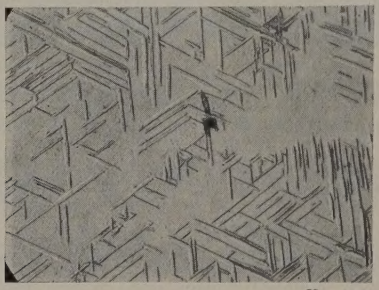
V = 3500

Abb. 1. TiAl6; 1 h 900°C/NaOH.



V = 3500

Abb. 2. TiAl6; 1 h 900°C/NaOH + 100 h 500°C/Luft.



V = 7000

Abb. 3. TiAl6; 1 h 900°C/NaOH + 100 h 500°C/Luft.

denen Partikel bei der Herstellung des Schliffes getroffen wird. Sie zeigen eine Orientierung gegenüber dem Grundmaterial. An der Legierung TiAl6V4 wurden ebenfalls bei elektronenmikroskopischen Untersuchungen Hinweise für die Ausscheidung dieser Phase in derselben Form festgestellt[9]. Die Bildung der α_2-Phase bei dieser Legierung war vorher nur durch Feinstrukturaufnahmen nachgewiesen worden[8]. Auch hier hatte die lichtmikroskopische Vergrößerung nicht ausgereicht,

* Frau Dr. E. PFEIFFER (Vacuumschmelze AG., Hanau) hat es freundlicherweise übernommen, die elektronenmikroskopischen Aufnahmen bei der Firma Siemens anzufertigen.

Literatur S. 184

die α_2-Phase neben der α-Phase – und in diesem Falle auch der β-Phase – aufzulösen. Bei einer Legierung mit 15% Al wurde bei elektronenmikroskopischen Untersuchungen eine ähnliche Ausbildung der α_2-Phase bei Temperaturen unter 1000°C in nahezu homogener Form beobachtet[7].

EINFLUß DER WÄRMEBEHANDLUNG AUF DIE VERSPRÖDUNG DURCH DIE α_2-PHASE

Betrachtet man das Dauerstandverhalten der aluminiumhaltigen Legierungen, so stellt man fest, daß zwischen 4 und 6% Al eine sehr erhebliche Verbesserung des Dauerstandverhaltens in der Wärme eintritt[1a]. Eine Legierung mit 8% Al zeigt aber, besonders beim Anlassen bei 550°C, eine starke Versprödung; bei einer Legierung mit 10% Al wurden nur spröde Brüche beobachtet[1a,1c]. Neben hohen Aluminiumgehalten können auch Eisen, Stickstoff, Sauerstoff und Wasserstoff zu einer

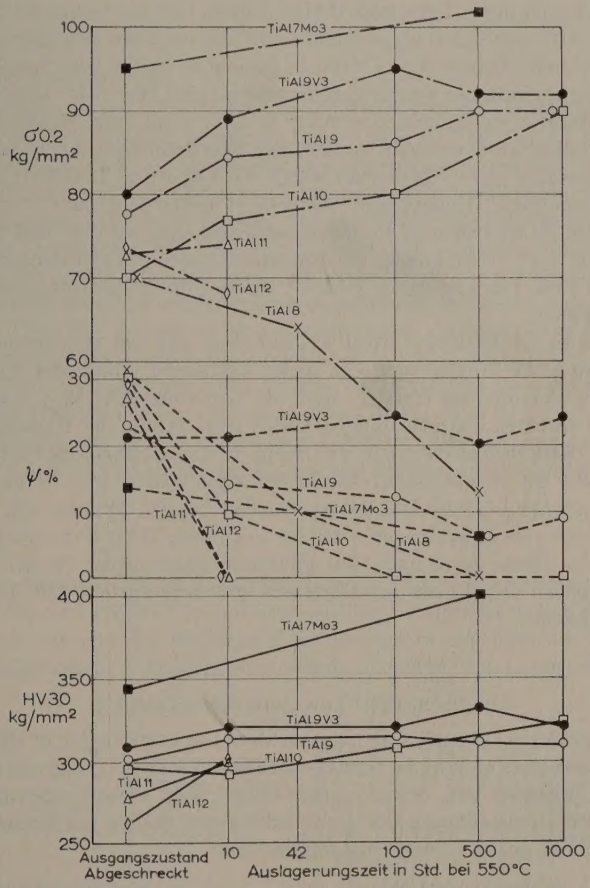


Abb. 4. Einfluß der Anlassdauer bei 550°C auf mech. Eigenschaften abgeschreckter Al-haltiger Ti-Legierungen.

Literatur S. 184

Versprödung der aluminiumhaltigen Titanlegierungen führen. Die Löslichkeit dieser Verunreinigungen in der Überstrukturphase und der Einfluß auf ihre Bildung sind noch nicht bekannt. Auf Grund des Einflusses von Stickstoff und Sauerstoff auf die Härte der Ti-Al-Legierungen[10] sind aber Änderungen im Gleichgewichtszustand zu erwarten. Untersuchungen an der Legierung TiAl7Mo3 haben weiterhin gezeigt, daß mit Zunahme der Umschmelzhärte des Titanschwammes die Versprödung bei Raumtemperatur stark zunimmt[1b].

Um einen Überblick über den Einfluß der Wärmebehandlungen auf Legierungen mit Gehalten von 8–12% Al zu gewinnen und die Wirkung von Zusätzen zu studieren, wurde eine Anzahl Legierungen durch zweimaliges Schmelzen mit Abschmelz-Elektrode im Hochvakuum hergestellt. Alle Legierungen wurden aus derselben Schwammsorte mit einer Umschmelzhärte von HB 30/10 = 100–110 kg/mm² erschmolzen und durch Strangpressen von 75 mm Dmr. auf 13 mm Dmr. in der gleichen Weise warmverformt. Die Legierungen TiAl9 und TiAl10 wurden von 900°C und die Legierungen TiAl11 und TiAl12 von 950°C abgeschreckt, um bei möglichst niedriger Glühtemperatur möglichst hohe Anteile der α_2-Phase in Lösung zu halten. Die Anlaßtemperatur betrug bei allen Legierungen 550°C. Vergleichsweise sind Werte der Legierung TiAl8, die aus der Literatur[1c] entnommen wurden, in Abb. 4 mit eingetragen. Diese Legierung ist aus Iodidtitan hergestellt worden. Die Abschrecktemperatur betrug 850°C, die Anlaßtemperatur 550°C. Fernerhin wurde die Legierung TiAl7Mo3, die als eine der besten warmfesten Legierungen weitgehend untersucht ist[1a–c], mit geprüft. Auf Grund zahlreicher eigener Untersuchungen hat sich ergeben, daß Legierungen mit 9% Al und 3–4% V besonders unempfindlich gegen verschiedenartige Wärmebehandlungen sind. Die Legierung TiAl9V3 ist deshalb in die Untersuchungen mit einbezogen worden.

Beim Vergleich der Meßwerte (Abb. 4) sieht man, daß mit zunehmendem Aluminiumgehalt durch die Auslagerung ein steiler werdender Abfall der Einschnürung und damit eine Versprödung eintritt. Auch die Legierung TiAl7Mo3 zeigt übereinstimmend mit früheren Untersuchungen[11] noch einen Abfall der Einschnürung. Der Grund dürfte darin liegen, daß sich, wie eigene Untersuchungen gezeigt haben, das Molybdän nicht im Mischkristall von Legierungen mit 6–9% Al löst, während Vanadin eine geringe Löslichkeit aufweist, die aber bei 9% Al unter 3% V liegt. Die Legierung TiAl9V3 ist deshalb noch – wie die Legierung TiAl7Mo3 – zu den $(\alpha + \beta)$-Legierungen des Titans zu rechnen. Die Phasenumwandlungen, die sich in TiAl9V3 bei 550°C abspielen und die aus der Härtezunahme hervorgehen, führen offenbar zu keiner Versprödung.

EIGENSCHAFTEN DER LEGIERUNG TiAl9V3

Aus einer größeren Anzahl von untersuchten Legierungen hatte die Legierung TiAl9V3 das geringste spezifische Gewicht und dabei sehr gute Eigenschaften in der Wärme. Im folgenden soll deshalb eingehender über diese Legierung berichtet werden. Die Zusammensetzung der an verschiedenen Stellen der Preßstangen entnommenen Proben ist in Tabelle I wiedergegeben*.

* Die Analysen wurden von der Analytischen Versuchs- und Beratungsstelle der Metallgesellschaft AG. ausgeführt.

Literatur S. 184

TABELLE I

ANALYSE VON VERSCHIEDENEN PREßSTANGEN DER LEGIERUNG TiAl9V3

Legierung	*Schmelz-Nr.*	*Al* %	*V* %	*Fe* %	*N* %	*O* %	*H* %
TiAl9V3	6761	A 8.47	2.92	0.041	0.009	0.05	0.0018
		E 8.50	2.84	0.057	0.010	0.06	0.0012
TiAl9V3	6942	A 8.61	2.91		0.007		
		E 8.70	2.97		0.012		
TiAl9V3	6950	A 8.46	2.91		0.008	0.06	0.0025
			2.84		0.011	0.07	0.0018
TiAl9V3	7080	A 8.58	2.92				
		E 8.63	2.94				

Einlegieren der Zusatzelemente

Untersuchungen an den Dreistoff-Systemen Ti-Al-V und Ti-Al-Mo haben gezeigt, daß im System Ti-Al-V keine geordnete Phase des CsCl-Typs im β-Gebiet auftritt, während das im System Ti-Al-Mo der Fall ist[12]. Beim Einlegieren von Vorlegierungen oder von Molybdän und Aluminium in Titan kann sich deshalb intermediär örtlich diese Zwischenphase bilden. Sie ist sehr spröde und hat möglicherweise einen hohen Schmelzpunkt. Zusammen mit dem an sich spezifisch schweren Molybdän löst sie sich nur sehr schwer im flüssigen Titan und hat deshalb die Tendenz auszuseigern. Durch röntgenographische Feinstrukturuntersuchungen von Seigerungen in Schmelzblöcken von TiAl7Mo3 konnte sie dort nachgewiesen werden. Demgegenüber lösen sich Vorlegierungen auf Ti-Al-V-Basis oder auch auf Al-V-Basis, die als Zusätze für das Erschmelzen der Legierung TiAl9V3 verwendet werden, wesentlich leichter im Titan, und zur Herstellung von homogenen Gußblöcken sind keine so hohen Stromstärken notwendig wie bei der Legierung TiAl7Mo3. Bei der Legierung TiAl9V3 wurden bisher in keinem Fall in Gußblöcken und Preßstangen Inhomogenitäten festgestellt.

Verformbarkeit

Die Warmverformbarkeit der Legierung TiAl9V3 wurde durch Strangpressen eines 75 mm Dmr. Barrens auf einer 400 t-Presse zu einer Stange von 13 mm Dmr. geprüft. Der Preßdruck während des gesamten Preßvorganges wurde über der Zeit in einem Diagramm aufgetragen. Vergleichsweise wurde auch das Diagramm der Legierung

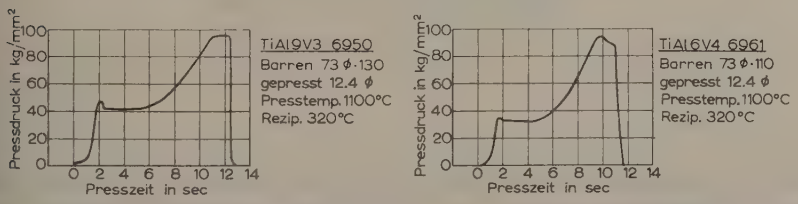


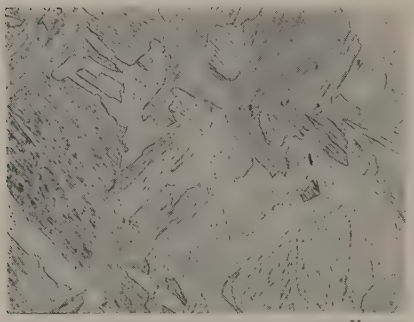
Abb. 5. Druckverlauf beim Strangpressen der Leg. TiAl9V3 u. TiAl6V4. Preßtemperatur 1100°C.

Literatur S. 184

$TiAl6V_4$ unter denselben Preßbedingungen aufgenommen. Abb. 5 zeigt die beiden Diagramme, aus denen ersichtlich ist, daß die Verformungsarbeit beim Strangpressen bei der Legierung $TiAl9V_3$ etwas größer ist als bei der Legierung $TiAl6V_4$. Strangepreßte Stangen aus $TiAl9V_3$ ließen sich mit Hilfe einer Hämmermaschine um 35% kaltverformen, ohne daß dabei eine Rißbildung auftrat.

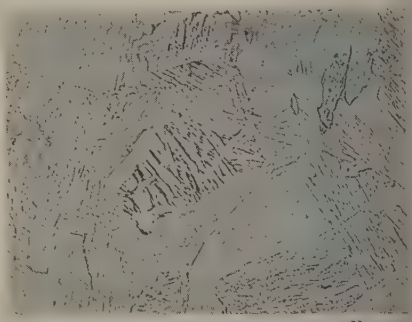
Mechanische Eigenschaften und Mikrogefüge

Die Eigenschaften der Legierung $TiAl9V_3$ wurden sowohl im Preßzustand als auch nach verschiedenen Wärmebehandlungen und nach Kaltverformung geprüft; sie sind in Tabelle II eingetragen. Es zeigt sich, daß die verschiedenartigen Wärmebehandlungen die mechanischen Eigenschaften nur wenig beeinflussen.



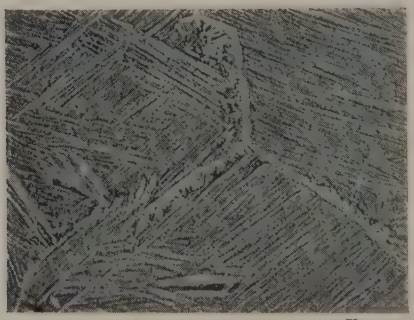
$V = 200$

Abb. 6. $TiAl9V_3$; 1/2 h 900°C/H_2O.



$V = 200$

Abb. 7. $TiAl9V_3$; 1/2 h 900°C/H_2O + 10 h 550°C/Luft.



$V = 400$

Abb. 8. $TiAl9V_3$; 2 h 700°C, 500°C/Luft + 25 kg/mm² 500°C 1000 h.

Auch die Gefügebilder zeigen nur geringe Unterschiede, was dadurch bedingt ist, daß die Phasen α und α_2 vorherrschen und auch bei hohen Temperaturen nur geringe Anteile der β-Phase vorhanden sind. Abb. 6 zeigt das Gefüge nach dem Abschrecken von 900°C und Abb. 7 nach der darauffolgenden Auslagerung von 10 h bei 550°C.

Literatur S. 184

TABELLE II

MECHANISCHE EIGENSCHAFTEN DER LEGIERUNG $TiAl_9V_3$

Schmelz-Nr.	*Prüftemp. °C*	*Vorbeh.*	*Wärmebeh.*	σB	$\sigma 0.2$	$\sigma 0.1$	$\sigma 0.05$	*E-Modul* $\times 10^3$	δ_5 %	ψ %	αK [a]	*HV 30*	
				kg/mm²							*mkg/cm²*	*Stirnfl.*	*Mantelfl.*
												kg/mm²	
6731	RT	Preßzust.	—	95.5	81.0	77.5	73.0	12.8	12.7	29.3	5.1	323 ±12	322 +9 −14
6731	RT	,,	1/2 h 900°C/H_2O	96.0	80.0	75.0	70.0	11.7	11.5	21.0	4.4	310 +5 −2	307 +8 −2
6761	RT	,,	1/2 h 900°C + 10 h 550°C/Luft	98.5	89.0	86.5	84.0	13.3	14.0	21.0	4.7	326 +9 −7	318 +5 −3
6761	RT	,,	1/2 h 900°C + 100 h 550°C/L	103.0	∼95.0	93.0	∼91.0	12.8	16.2	24.0	n.b.	334 +14 −8	306 +10 −7
6761	RT	,,	1/2 h 900°C + 500 h 550°C/L	98.3	91.5	n.b.	86.0	12.5	12.5	20.0	n.b.	343 +18 −20	320 +5 −6
6761	RT	,,	1/2 h 900°C + 1000 h 550°C/L	99.2	>92.0	n.b.	>90.0	12.6	12.7	24.0	n.b.	327 +7 −7	316 +15 −18
6761	RT	,,	1/2 h 900°C/H_2O + 1000 h 450°C/L	91.8	∼82.0	∼81.0	∼77.0	12.5	16.2	29.0	n.b.	313 +8 −5	310 +5 −6
6761	RT	,,	2 h 700°C/Ofenabk. 500°C/L	102.0	92.0	89.0	87.0	13.1	12.7	25.0	n.b.	318 +5 −7	325 +10 −6
6942	RT	,,	,,	104.0	∼98.0	n.b.	n.b.	12.8	11.5	16.0	n.b.	340 +24 −31	318 +3 −2
7225	RT	,,	,,	90.8	76.0	71.6	66.5	12.5	14.8	32.0	n.b.	310 +7 −8	312 +2 −1
7225	500°C	,,	,,	58.1	45.3	41.7	38.0	9.5	20.0	43.7	n.b.	n.b.	n.b.
7225	550°C	,,	,,	57.8	45.3	41.5	38.0	10.3	19.5	58.7	n.b.	n.b.	n.b.
7225	RT	Preßzustand + 35% Kaltverf.	—	126.3	111.8	103.0	93.0	10.6	6.7	18.7	n.b.	345 +3 −2	373 +6 −3

[a] 5 mkg, Auflage 40 mm 5.5 × 8.5 mm.

Abb. 8 gibt das Gefüge wieder, das nach einer Vorglühung von 2 h bei 700°C/Ofenabkühlung auf 500°C/Luftabkühlung und anschließender Zeitstandbeanspruchung von 25 kg/mm² über 1000 h bei 500°C entstanden ist. Es dürfte etwa dem des Gleichgewichtszustandes entsprechen. Es sind noch deutlich sichtbare Anteile der dunkel angeätzten β-Phase vorhanden.

Einfluß des Wasserstoffs auf das Dauerstandverhalten gekerbter Proben bei Raumtemperatur

Gehalte an Wasserstoff machen sich bei ($\alpha + \beta$)-Titanlegierungen während des Dauerstandversuches bei Raumtemperatur an gekerbten Proben dadurch im all-

TABELLE III

ZEITSTANDVERSUCHE MIT GEKERBTEN PROBEN DER LEGIERUNG TiAl9V3 BEI RAUMTEMPERATUR

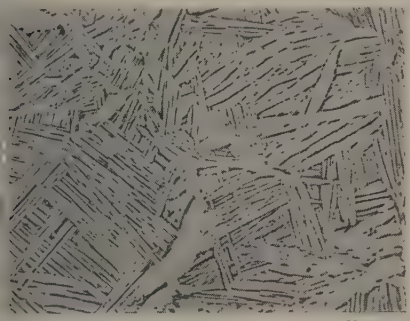
Probenabmessungen: Durchmesser im Kerbgrund 4 mm, Kerbradius 0.01 mm, Kerbwinkel 60°, Kerbtiefe 1 mm.
Wärmebehandlung: Im Vak. 1/2 h 900°C in 20 min auf 700°C, 1 h 700°C/Ofen ab 500°C/Vak.

Schmelz-Nr.	*Zusatz H_2 in Gew.-%*	*Beanspruchung und Lastdauer in kg/mm² / Stunden (Bruch)*	*Izod-kerbschlagz. cmkg/mm²* [c]
6761	0	80 kg/mm² 5000 h + 85 kg/mm² 22 h B	
6761	0	90 kg/mm² 19.4 h B	
6761	0	110 kg/mm² 3.3 h B	
7080[a]	0	85 kg/mm² 5.3 h B	2.61
7080[a]	0	85 kg/mm² 573 h B	3.01
7080	0.0034	65 bis 120 kg/mm² [b] je 100 h + 125 kg/mm² 0.5 h B	2.31
7080	0.0034	115 kg/mm² 7.3 h B	2.21
7080	0.016	65 bis 120 kg/mm² [b] je 100 h + 125 kg/mm² 0 h B	1.99
7080	0.016	115 kg/mm² 2838 h + 125 kg/mm² 35 h B	
7080	0.036	65 bis 120 kg/mm² [b] je 100 h + 125 kg/mm² 0 h B	1.43
7080	0.036	115 kg/mm² 2838 h + 125 kg/mm² 11 h B	
7080	0.055	65 bis 120 kg/mm² [b] je 100 h + 125 kg/mm² 0 h B	1.91
7080	0.055	115 kg/mm² 7.3 h B	1.70
6761	0.1	60 kg/mm² 789 h + 70 kg/mm² 0 h B	
7080	0.1	65 bis 100 kg/mm² [b] je 100 h + 105 kg/mm² 36 h B	1.27
6761	0.1	65 bis 80 kg/mm² [b] je 1000 h + 90 kg/mm² 2000 h + 95 kg/mm² 0 h B	
7080	0.1	95 kg/mm² 3170 h + 105 kg/mm² 100 h B	
7080	0.29	65 kg/mm² 0 h B	0.238
7080	0.29	40 bis 45 kg/mm² [b] je rd. 100 h + 50 kg/mm² 0 h B	0.318
6761	0.57	65 kg/mm² 0 h B	
6761	0.57	90 kg/mm² 0 h B	

[a] Nur 2 h 700°C/Ofen ab 500°C/Luft.
[b] Beanspruchung um je 5 kg/mm² erhöht.
[c] Nach Beendigung des Zeitstandversuchs.

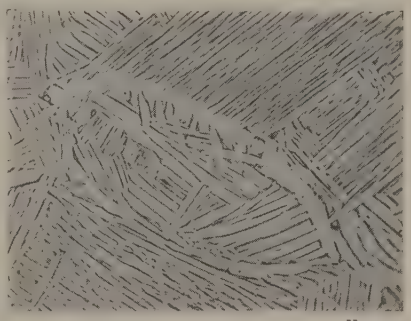
Literatur S. 184

gemeinen unangenehm bemerkbar, daß die Zeitbruchfestigkeit bereits bei kleinen Gehalten stark abfällt[13,14]. Im Laufe einer Beanspruchung bei hohen Temperaturen ist aber mit einer – wenn auch geringen – Wasserstoffaufnahme bei Titanlegierungen zu rechnen. Die Wasserstoffaufnahme aus dem Wasserdampf der Luft (bei 21°C mit etwa 35% an Wasserdampf gesättigt) wurde bei einer Dauerstandbeanspruchung von 500 h bei 550°C und einer Belastung von 25 kg/mm² an der Legierung $TiAl_9V_3$ gemessen. Die Probe enthielt vor dem Dauerstandversuch 0.0015% H_2 und nach dem Versuch über 500 h mit einer Beanspruchung von 25 kg/mm² bei 550°C 0.0025% H_2. Der Einfluß des Wasserstoffs auf das Dauerstandverhalten gekerbter Proben bei Raumtemperatur wurde deshalb geprüft.



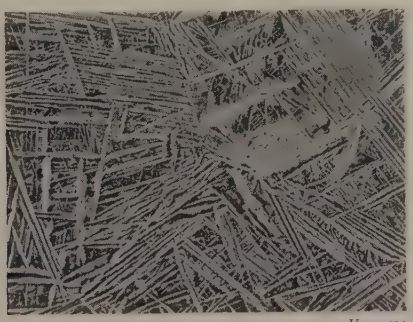
V = 400

Abb. 9. $TiAl_9V_3$; 1/2 h 900°C, 1 h 700°C, 500°C/Vakuumabkühlung.



V = 400

Abb. 10. $TiAl_9V_3$; 1/2 h 900°C, 1 h 700°C, 500°C/Vakuumabkühlung + 0.1 Gew.-% H_2.



V = 400

Abb. 11. $TiAl_9V_3$; 1/2 h 900°C, 1 h 700°C, 500°C/Vakuumabkühlung + 0.29 Gew.-% H_2.

Die Vorbehandlung der wasserstoffreien Vergleichsproben entsprach derjenigen der mit Wasserstoff beladenen Proben und war wie folgt: 1/2 h 900 C, in 20 min Ofenabkühlung auf 700°C, 1 h 700 C, Ofenabkühlung auf 500 C, weitere Abkühlung auf Raumtemperatur. Tabelle III gibt die Ergebnisse dieser Versuche wieder. Danach wird durch Gehalte von etwa 0.004 bis 0.04% H_2 die Zeitstandfestigkeit gekerbter

Literatur S. 184

Proben bei einer Prüfdauer von über 1000 h gegenüber wasserstoffreien Proben von 80 auf 115 kg/mm² erhöht. Erst bei Gehalten von etwa 0.1% H_2 fällt die Zeitstandfestigkeit unter die des wasserstoff-freien Materials ab.

Die Legierung TiAl9V3 zeigt zwar eine geringere Dauerstandfestigkeit im gekerbten Zustand nach dieser Wärmebehandlung als andere ($\alpha + \beta$)-Legierungen[14], ist aber weit weniger empfindlich gegen Gehalte an Wasserstoff. Dies dürfte in erster Linie auf eine größere Löslichkeit für Wasserstoff bei Raumtemperatur zurückzuführen sein. Untersuchungen über die Löslichkeit des Wasserstoffs bei Ti-Al-Legierungen haben gezeigt, daß mit 5% Al und bei höheren Gehalten an Aluminium die Löslichkeit bei Raumtemperatur beträchtlich zunimmt und daß die versprödende Wirkung des Wasserstoffs erst bei viel höherem Wasserstoffgehalt merkbar wird als dies bei geringeren Gehalten an Aluminium der Fall ist. So fällt auch die Kerbschlagzähigkeit der Legierungen mit 5 und 7% Al erst bei höheren Wasserstoffgehalten ab als bei Reintitan und einer Legierung mit 2% Al[15–17].

Die starke Gefügeänderung, die bei Gehalten von über 0.1% H_2 auftritt, ist aus den Abbildungen 9 bis 11 zu ersehen. Durch die langsame Abkühlung ist im wasserstoffreien Zustand annähernd der Gleichgewichtszustand erreicht (Abb. 9). Ein Gehalt von 0.1% H_2 ändert an der Art der Gefügeausbildung nur wenig (Abb. 10). Ein Gehalt von 0.29% H_2 (Abb. 11) verursacht eine plattenförmige Ausscheidung der α-Phase, die offenbar innere Kerben darstellen und infolgedessen die Zeitstandfestigkeit verringern.

Ein Teil der Proben war mit zwei Kerben versehen worden. Diese Proben wurden nach dem Dauerstandversuch in der nicht gebrochenen Kerbe abgeschlagen. Die Ergebnisse sind in Tabelle III eingetragen. Erst bei Gehalten von über 0.1% H_2 ist mit einem starken Abfall der Kerbschlagzähigkeit zu rechnen. Ein Einfluß der Zeit der Vorbelastung konnte nicht sicher nachgewiesen werden.

Zeitstandverhalten bei höheren Temperaturen

Um die Proben in einem möglichst stabilen Zustand zu prüfen, wurde das Zeitstandverhalten nach einer Glühung von 2 h 700°C/Ofenabkühlung auf 500°C und

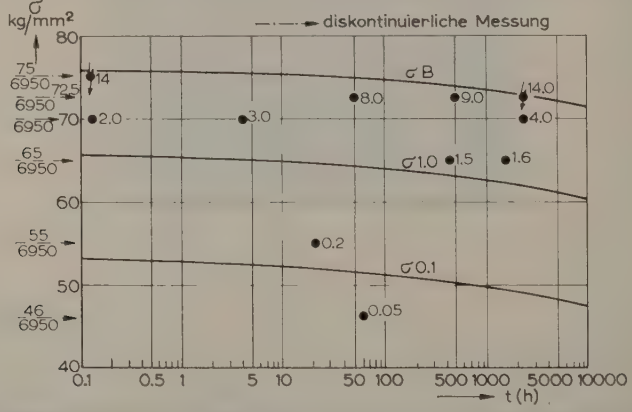


Abb. 12. Dauerstandverhalten der Leg. TiAl9V3 bei 350°C. (Die grossen Zahlen an der ordinate sind Chargen-Bezeichnungen.)

Literatur S. 184

anschließender Luftabkühlung gemessen. Die Versuche erfolgten bei 350°, 450°, 500° und 550°C. Bei geringen Lasten wurde die Dehnung im allgemeinen mit Martens-Spiegelgeräten laufend gemessen, während höher belastete Proben nach bestimmten Versuchszeiten für die Messung ausgebaut wurden.

Bei der Prüftemperatur von 350°C wurden die Proben nach jeweils etwa 100, 250, 500 und 1000 h ausgebaut. Bei keiner Probe wurde kontinuierlich gemessen. Die Ergebnisse dieser Versuche sind in Abb. 12 dargestellt. Je nach Belastung tritt bei 350°C noch eine erhebliche Verfestigung und dadurch ein hoher Kriechwiderstand auf. So ging bei einer Beanspruchung von 75 kg/mm² eine Probe sofort mit 14% Dehnung zu Bruch, während eine andere Probe bei 72.5 kg/mm² erst nach 2000 h eine Dehnung von 13% aufwies. Unter 65 kg/mm² Beanspruchung nahm die Dehnung zwischen der 500. und 1500. Stunde nur von 1.5 auf 1.61% zu. Die Zeitdehngrenze σ 0.1/1000 beträgt etwa 48 kg/mm².

Bei 450°C beträgt die Zeitstandfestigkeit σ B/1000 etwa 58 kg/mm² und die Zeitdehngrenze σ 0.1/1000 etwa 30 kg/mm² (Abb. 13). Geringe Unterschiede in der Legierungszusammensetzung machen sich bei den kleinen Dehngrenzen stark bemerkbar.

Bei 500°C beträgt die Zeitstandfestigkeit σ B/1000 40 kg/mm² für die Zeitdehngrenze σ 0.1/1000 20 kg/mm² (Abb. 14). Bei 550°C erfolgt ein Bruch nach 1000 h unter einer Beanspruchung von 29 kg/mm² und eine Dehnung von 0.1% nach 1000 h unter einer Beanspruchung von 15 kg/mm² (Abb. 15).

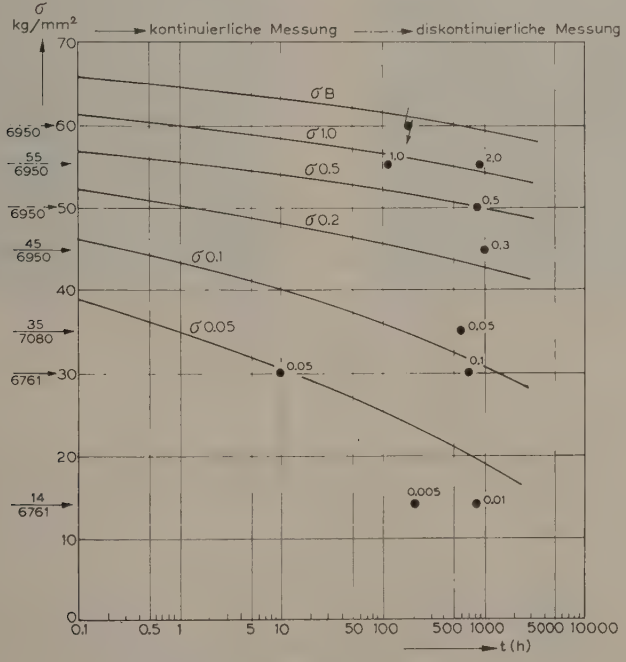


Abb. 13. Dauerstandverhalten der Leg. TiAl9V3 bei 450°C.

Literatur S. 184

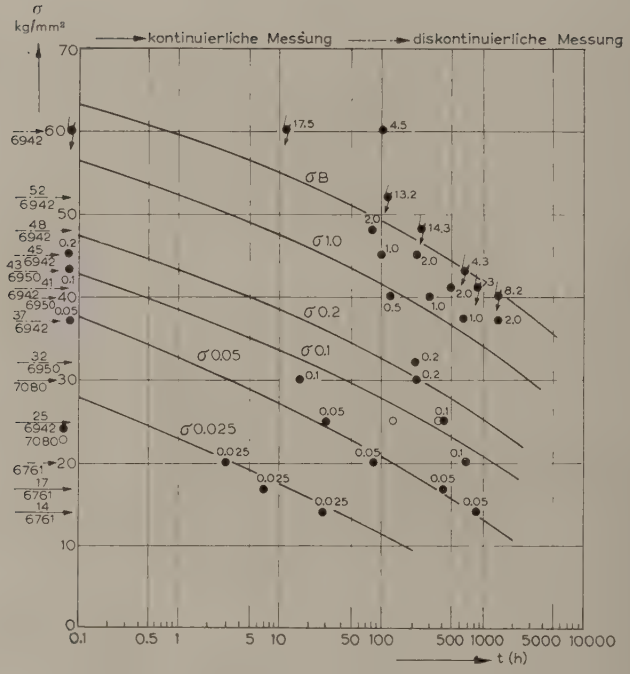


Abb. 14. Dauerstandverhalten der Leg. TiAl9V3 bei 500°C.

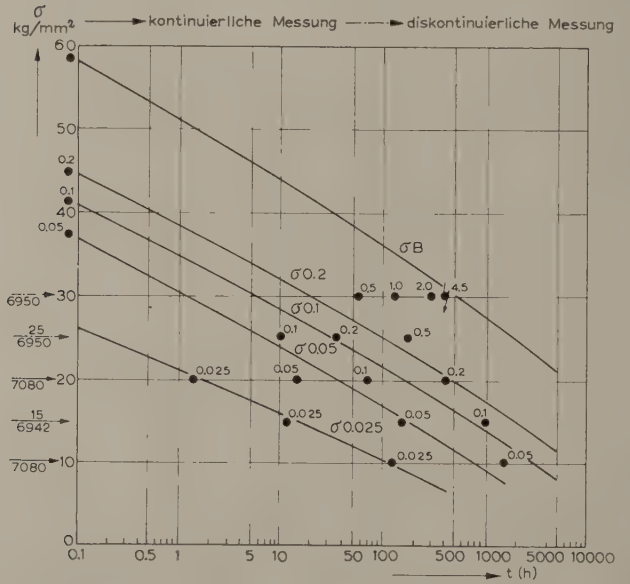


Abb. 15. Dauerstandverhalten der Leg. TiAl9V3 bei 550°C.

Mechanische Eigenschaften nach Dauerbeanspruchung

Nach einer Dauerstandbeanspruchung bei erhöhter Temperatur bleiben die mechanischen Eigenschaften der Proben bei Prüfung bei Raumtemperatur nur dann unverändert, wenn eine Temperatur von 400°C oder bei 450° und 500°C die Zeitdehngrenze $\sigma_{0.2/1000}$ nicht überschritten wird. Unter höheren Beanspruchungen und Temperaturen findet man manchmal eine örtliche Auflockerung des Gefüges, die von der

Abb. 16. TiAl9V3; 37 kg/mm² 500°C 2000 h, $\delta = 2.4\%$.

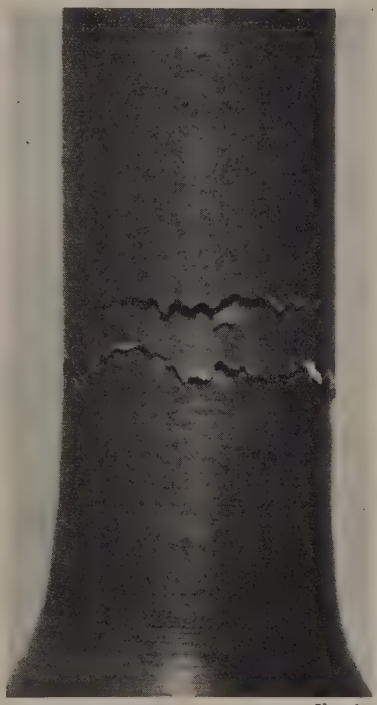


Abb. 17. TiAl9V3; 30 kg/mm² 550°C, nach 343 h Bruch mit $\delta = 4.5\%$.

robenoberfläche ausgeht und sich entlang der Kornzwischensubstanz fortsetzt. erartige Erscheinungen werden auch an anderen warmfesten Titanlegierungen obachtet[18,19]. Man nimmt an, daß eine Art Spannungskorrosion, die durch salztige Verbindungen entstehen kann, die Ursache für dieses Verhalten ist. Abb. 16 igt eine Probe, die mit 37 kg/mm² bei 500°C 2000 h lang belastet war und eine ehnung von 2.4% erreichte. An leicht oxydierten und korrodierten Stellen bilden ch kleine Risse, die sich entlang der Korngrenzen fortsetzen. Im Innern der Probe ird noch keine Auflockerung des Gefüges beobachtet. Abb. 17 gibt eine Probe ieder, die bei 550°C und einer Belastung von 30 kg/mm² nach 343 h mit 4.5%

iteratur S. 184

Dehnung gebrochen war. Man sieht deutlich die Auflockerung des Gefüges durch die Rißbildung an den Korngrenzen. Bei 350°C werden auch nach 2000 h unter 72.5 kg/mm² Belastung noch keine Anzeichen einer derartigen Rißbildung beobachtet.

Izod-Proben wiesen im Ausgangszustand eine Kerbschlagzähigkeit von 2.8 $^{+0.3}_{-0.4}$ cmkg/mm² auf. Nach einer Dauerstandbeanspruchung von 25 kg/mm² bei 500°C über 1000 h, wobei die Probe um 0.13% gedehnt wurde, betrug die Kerbschlagzähigkeit noch 2.6 cmkg/mm².

Tabelle IV gibt die Ergebnisse von Proben wieder, die nach der Dauerstandbeanspruchung bei Raumtemperatur im Zugversuch zerrissen wurden. Übersteigen die Versuchsbedingungen die oben angeführten Beanspruchungsgrenzen, so ist mit einer Versprödung zu rechnen.

TABELLE IV

Schmelz-Nr.	Prüftemp. °C	Beanspruchung kg/mm²	Zeit h	Bleib. Dehnung %	Mechanische Eigenschaften nach Dauerstandversuch			
					σ B kg/mm²	σ 0.2 kg/mm²	δ 5 %	ψ %
6950	350	46.0	250	0.064	95.0	n.b.	15.3	26.5
6950	350	55.0	250	0.28	94.6	n.b.	16.0	29.0
6950	350	65.0	1506	1.6	n.b.	n.b.	n.b.	n.b.
6950	350	70.0	2078	3.92	98.0	n.b.	10.3	25.6
6950	350	72.5	2000	13.3	110.0	n.b.	3.7	17.5
6950	350	75.0	1′	13.96	während des Versuchs gebrochen			
6761	450	14.0	500	0.008	90.7	83.2	16.0	31.0
6761	450	30.0	1000	0.144	90.0	84.0	13.2	18.0
7080	450	35.0	500	0.045	95.0	91.2	7.0	8.0
6950	450	45.0	500	0.33	91.3	n.b.	2.5	—
6950	450	50.0	849	0.57	98.5	n.b.	5.3	8.8
6950	450	55.0	849	2.40	93.4	n.b.	3.0	6.0
6950	450	60.0	174	11.6	während des Versuchs gebrochen			
6761	500	14.0	961	0.05	95.8	91.4	10.7	13.0
6761	500	17.0	649	0.05	93.0	89.0	16.5	21.3
6761	500	20.0	1000	0.09	92.3	87.5	16.5	22.4
6942	500	25.0	1000	0.13	93.9	91.5	1.8[a]	—
7080	500	25.0	574	0.12	98.0	94.8	10.6	13.5
7080	500	30.0	500	0.27	95.6	n.b.	8.0	12.4
6950	500	32.0	229	0.2	n.b.	n.b.	n.b.	n.b.
6942	500	37.0	2000	2.46				
6950	500	40.0	1205	3.4				
6950	500	41.0	708	3.0[a]				
6950	500	43.5	556	4.3	während des Versuchs gebrochen			
6942	500	45.5	204	2.0				
6942	500	48.0	219	8.86				
6942	500	52.0	122	11.78				
6942	500	60.0	117	4.57	Rißbildung an der Oberfläche			
6942	500	60.0	15	17.5	während des Versuchs gebrochen			
7080	550	10.0	226	0.024	92.3	91.3	2.8	4.5
6942	550	15.0	1000	0.20	92.0	n.b.	2.3	n.b.
7080	550	20.0	500	0.20	92.5	92.3	0.5	n.b.
6950	550	25.0	483	0.5	96.0	91.0	2.5	8.5
6950	550	30.0	343	4.5	während des Versuchs gebrochen			

[a] An Fehlstelle gebrochen.

Literatur S. 184

Wechselfestigkeit

Die Wechselfestigkeit wurde nur an Proben untersucht, die nach 2 h 700°C, Ofenabkühlung auf 500°C, Luftabkühlung, weichgeglüht worden waren. Die Biegewechselfestigkeit glatter Proben beträgt σ bw $= \pm$ 42 kg/mm² und die gekerbter Proben* Abb. 18a) $\pm$ 14 kg/mm². Um ein Verhämmern von unter Zugdruckbeanspruchung u Bruch gehenden Proben zu vermeiden, wurde bei dieser Beanspruchungsart immer ine Zugvorspannung von + 3 kg/mm² aufgebracht. Unter dieser Bedingung beträgt ie Zugdruckwechselfestigkeit glatter Proben bei Raumtemperatur σ zd $= 3 \pm 36$ g/mm² und die gekerbter Proben 3 $\pm$ 12 kg/mm² (Abb. 18 b).

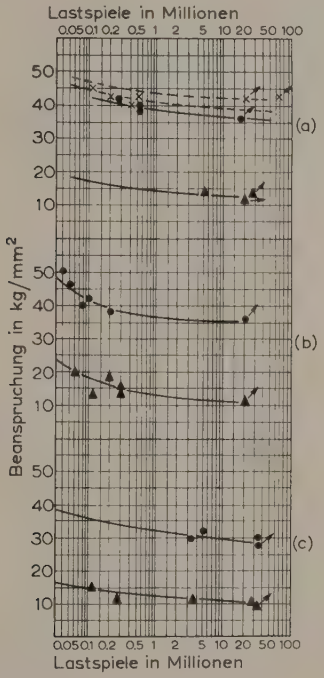


Abb. 18. Wechselfestigkeit auf Basis $20 \cdot 10^6$ Lastspielen bei RT und 450°C.

Abb. 18a.
TiAl9V3 6950; σ bw RT $\pm$ 38–42 kg/mm²
TiAl9V3 7225; σ bw RT $\pm$ 36 kg/mm² glatt
TiAl9V3 7225; σ bw RT $\pm$ 14 kg/mm² gekerbt

Abb. 18b.
● TiAl9V3 6942; σ zd RT 3 $\pm$ 35 kg/mm² glatt
▲ TiAl9V3 7080; σ zd RT 3 $\pm$ 12 kg/mm² gekerbt

Abb. 18c.
● TiAl9V3 6942; σ zd 450°C 3 $\pm$ 29 kg/mm² glatt
▲ TiAl9V3 7080; σ zd 450°C 3 $\pm$ 11 kg/mm² gekerbt

* Kerbradius rd. 0.05 mm, Kerbwinkel 60°, Probendurchmesser im Kerbgrund 5 mm, Probenurchmesser glatter Proben 5 mm.

teratur S. 184

Bei 450 C beträgt die Zugdruckwechselfestigkeit glatter Proben noch 3 ± 29 kg/mm² und die der gekerbten Proben 3 ± 11 kg/mm² (Abb. 18 c). Im Dauerstandversuch wurde bei einer Belastung von 29 kg/mm² und bei 450 C etwa die Zeitdehngrenze σ 0.1/1000 erreicht.

Versprödung gekerbter Proben in der Wärme

Versprödungserscheinungen während der Zeitstandbeanspruchung in der Wärme kann man mit gekerbten Proben im Vergleich mit glatten Proben nachweisen. Bei verschiedenen Temperaturen und Belastungen wurden deshalb unter gleichen Bedingungen einige Zeitstandversuche mit glatten und gekerbten Proben* ausgeführt. Die Ergebnisse dieser Versuche sind in Tabelle V zusammengefaßt. Sie zeigen, daß

TABELLE V

Schmelz-Nr.	*Form*	*Prüftemperatur °C*	*Beanspruchung kg/mm²*	*Bruch nach Stunden*
6950	gekerbt	550	30	50
6950	glatt	550	30	343
6950	gekerbt	500	43.5	549
6950	glatt	500	43.5	550
6950	gekerbt	500	40	880
6950	glatt	500	40	1205

bei 500 bis 550 C und der Beanspruchungsdauer von rd. 1000 h sich glatte und gekerbte Proben innerhalb der Fehlergrenze gleichartig verhalten. Bei längeren Beanspruchungen ist aber zu befürchten, daß durch die oben beschriebene Rißbildung ein vorzeitiger Bruch gekerbter Proben eintritt. Bei der Legierung TiAl6V4 wurde im weichgeglühten Zustand ebenfalls ein rascheres Absinken der Zeitbruchfestigkeit gekerbter Proben bei 510 C gefunden als dies bei glatten Proben und tieferen Temperaturen der Fall war[20].

VERZUNDERUNG VERSCHIEDENER ALUMINIUMHALTIGER UND WARMFESTER TITANLEGIERUNGEN

Bei den Titanlegierungen macht sich die starke Aufnahme von Gasen – insbesondere von Sauerstoff aus der Luft – bei höheren Temperaturen unangenehm bemerkbar. Um zu prüfen, wie stark die Legierung TiAl6V3 bei Erwärmung auf Warmverformungstemperaturen gegenüber dem Angriff von Luft empfindlich ist, wurden an einigen Proben die Gewichtszunahmen an Luft bei 600°, 700° und 950°C (Abb. 19 und 20, Tabelle VI) gemessen.

Als Proben dienten scheibenförmige Körper mit einer Oberfläche von durchschnittlich 3 cm² bei einem Durchmesser von 12 mm und einer Höhe von etwa 3 mm. Die Proben wurden in unglasierten Porzellantiegeln bei Temperaturen von 600°, 700° und 950 C an Luft im Elektroofen geglüht. Vergleichsweise wurden einige weitere warmfeste Legierungen, Reintitan und binäre Ti-Al-Legierungen mitgeglüht. Die Ergebnisse sind in den Abbildungen 19 und 20 wiedergegeben. Bei allen Temperaturen

* Kerbradius rd. 0.05 mm, Kerbwinkel 60°, Kerbtiefe 1 mm.

Literatur S. 184

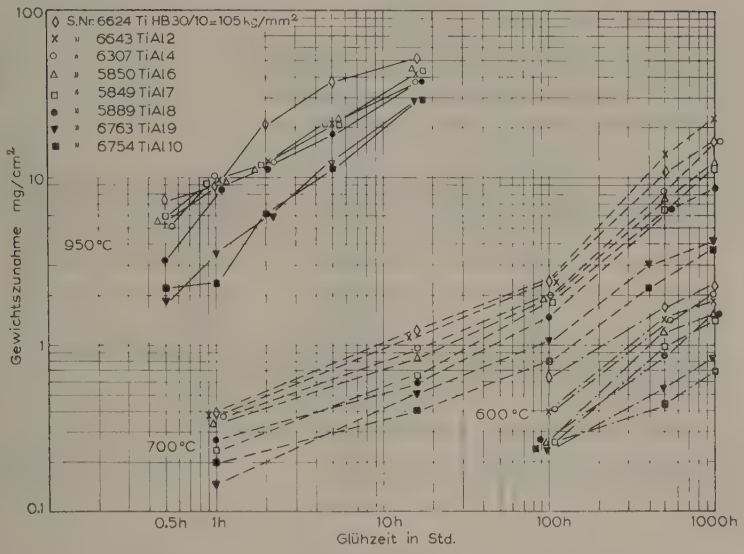


Abb. 19. Verzunderung von Ti-Al-Legierungen bei 600°C, 700°C, und 950°C.

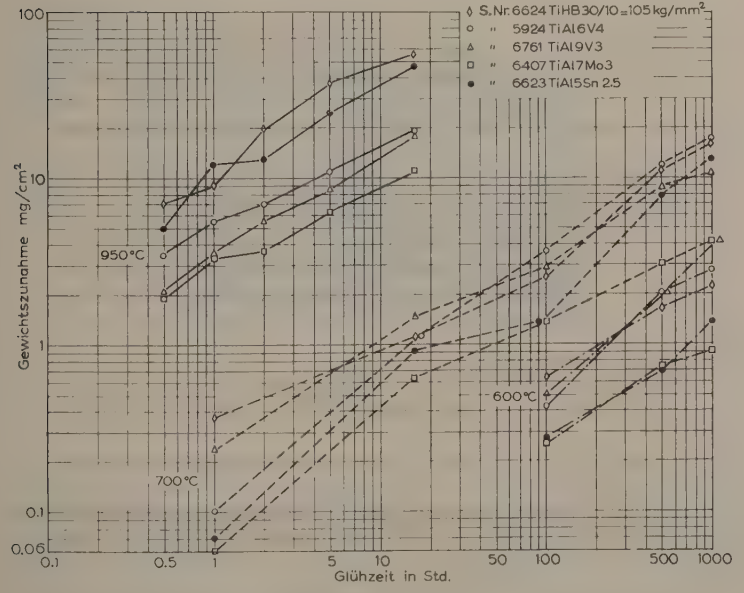


Abb. 20. Verzunderung verschiedener Ti-Leg. bei 600°C, 700°C, und 950°C.

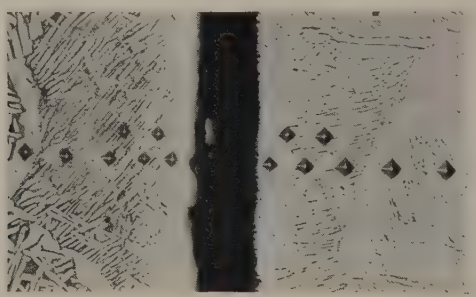
TABELLE VI

GEWICHTSZUNAHME IN mg/cm²

Schmelz-Nr.	*Legierung*	*1000 Std. 600°C*	*1000 Std. 700°C*	*16 Std. 950°C*
6624	Ti, Osaka SA	2.27	16.9	52.5
6643	TiAl2	1.86	21.6	38.6
6307	TiAl4	2.03	17.0	41.5
5850	TiAl6	1.55	12.3	44.8
5849	TiAl7	1.43	11.7	44.5
5889	TiAl8	1.66	8.6	39.1
6763	TiAl9	0.83	4.1	29.7
6754	TiAl10	0.71	3.75	30.4
5924	TiAl6V4	2.71	18.3	19.7
6761	TiAl9V3	4.40	11.0	18.1
6407	TiAl7Mo3	0.94	4.30	11.3
6623	TiAl5Sn2.5	1.40	11.9	48.3

und bei den längsten Expositionszeiten verzunderten die Ti-Al-Legierungen weniger als Reintitan. Innerhalb der Ti-Al-Legierungen zeigt sich zwischen 8 und 9% Al ein deutlicher Sprung zu einer geringeren Gewichtszunahme. Die Temperaturen und Konzentrationen fallen mit der Bildung der α_2-Phase zusammen, durch die wahrscheinlich die Diffusions- und Verzunderungsvorgänge gehemmt werden.

Bei allen vanadiumhaltigen Legierungen wurde bei 950°C eine starke gelbbraune Färbung des Tiegels beobachtet. Eine Bestimmung des Vanadiumgehaltes der Legie-



V 200

Abb. 21. Diffusionszonen der Legierung TiAl9V3 (rechts 50 μ) und TiAl6V4 (links 150 μ) nach einer Glühung von 2 h bei 950°C an Luft.

rung TiAl9V3 ergab vor der Verzunderung 2.92% V und nach einer Glühung von 5 h bei 950°C an Luft einen Gehalt von 2.79% V. Die Abnahme des Vanadiumgehaltes und die Färbung des Tiegels sind auf eine Verdampfung dieses Legierungselementes aus der Oxydschicht in Form von V_2O_5 zurückzuführen. Die Legierung TiAl7Mo3 zeigt insbesondere bei hohen Temperaturen eine anscheinend sehr geringe

Literatur S. 184

Gewichtszunahme. Dies ist in erster Linie darauf zurückzuführen, daß das Molybdän in Form von MoO_3 die Neigung hat, noch viel stärker zu verdampfen als Vanadium in Form von V_2O_5. Bei den warmfesten Titanlegierungen zeigt die Legierung TiAl6V4 im Durchschnitt etwa dieselbe Gewichtszunahme wie die Legierung TiAl9V3.

Abb. 21 zeigt die Diffusionszonen dieser beiden Legierungen nach einer Glühung von 2 h 950°C. Der Abfall der Mikrohärte erreicht bei TiAl6V4 erst nach 150 μ Diffusionszone den Wert der Grundmasse, während bei TiAl9V3 dieser Wert bereits nach 50 μ erreicht wird. Beim Entzundern muß deshalb bei der Legierung TiAl9V3 keine so dicke Schicht abgetragen werden wie bei der Legierung TiAl6V4.

VERGLEICH DES DAUERSTANDVERHALTENS VERSCHIEDENER WARMFESTER TITANLEGIERUNGEN

Auf Grund der bisher beschriebenen Untersuchungen scheint bis zu Betriebszeiten von etwa 2000 h eine Dauerstandbeanspruchung von warmfesten Titanlegierungen bis zu etwa 450°C und 30 kg/mm² Belastung möglich, ohne daß die Gefahr eines Sprödbruches nach Abkühlen auf Raumtemperatur oder bei erhöhter Temperatur zu befürchten ist. Um verschiedene warmfeste Titanlegierungen miteinander zu ver-

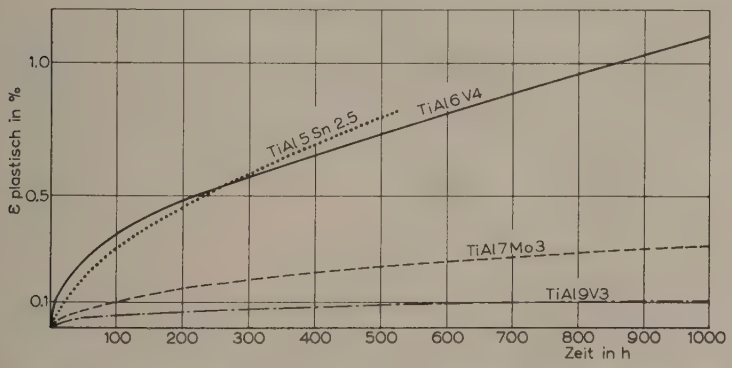


Abb. 22. Kriechkurven bei einer Belastung von 30 kg/mm² und einer Temperatur von 450°C.
– – – – TiAl7Mo3
—·—·— TiAl9V3
····· TiAl5Sn2.5
—— TiAl6V4
} stranggepreßt 2 h 700°C/Ofenabkühlg. auf 500°C/Luft.

gleichen, wurden die Legierungen TiAl5Sn2.5, TiAl6V4 und TiAl7Mo3, die für gutes Dauerstandverhalten bei hoher Temperatur bekannt sind, mit der Legierung TiAl9V3 verglichen. Als Belastung bei einer Temperatur von 450°C wurde 30 kg/mm² gewählt. Die Messungen erfolgten kontinuierlich. Abb. 22 gibt die bleibende Dehnung in Abhängigkeit von der Zeit bis 1000 h wieder. Demnach zeigt die Legierung TiAl9V3 unter dieser Beanspruchung das beste Dauerstandverhalten.

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THE AVAILABILITY, RECOVERY AND PROPERTIES OF RHENIUM METAL

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SUMMARY

Rhenium, a relatively new and unknown metal, is inherently rare and probably will continue to be expensive. However, at least a few thousand pounds can be readily obtained yearly as a by-product from molybdenum concentrates. Its extremely high melting point and good metal properties indicate a growing use for those applications where a relatively high cost can be tolerated. Uses in the electronics industry, as an electrical contact material, alloyed with tungsten and with molybdenum, and for high temperature thermocouples are among potential industrial applications.

INTRODUCTION

The continued need for improved high-temperature materials has prompted consideration of rhenium for special applications despite its scarcity and high cost.

Rhenium's high melting point (3180°C) and relatively low vapor pressure have been primarily responsible for the attention it has received in recent years, but it has several other properties that distinguish it from its chief competitors among the refractory metals.

(1) Rhenium is the most refractory of the metals that can be electrodeposited from aqueous solution.

(2) Rhenium is markedly superior to tungsten[1] with respect to resistance to attack resulting from transfer by the "water cycle".

(3) Rhenium has a low contact resistance[1].

(4) Rhenium does not form stable carbides[2].

(5) Rhenium has better room temperature ductility than tungsten.

(6) Rhenium has good thermoelectric properties.

While other properties could be noted, these, together with its high melting point, are considered most significant from the standpoint of potential commercial applications of the metal.

References p. 191

AVAILABILITY

Rhenium was discovered in 1925 by the German chemists NODDACK, TACKE and BERG but attracted little attention outside of Germany because the only known workable deposits were at Mansfeld, Germany.

Rhenium will, in all likelihood, always remain a scarce metal. However, deposits of commercial interest are now found in the United States, Chile and the U.S.S.R., as well as in Germany.

Analyses of numerous minerals have indicated that the rhenium content of the earth's crust is about the same as some of the platinum group metals. Thus, it is fundamentally one of the really rare metals, although it may be found in concentrations that make it more readily available than some metals of the platinum group.

Rhenium is found in nature principally as the disulfide in molybdenite ores. The rhenium content of molybdenite varies widely, *i.e.*, from less than one part per million to occasional samples reportedly containing several per cent. At present, a molybdenite concentrate containing 0.03 to 0.08 per cent rhenium is considered to be a very promising source. A handicap in determining the availability of rhenium has been the difficulty of analysis, particularly when it is present in very low concentration, and many analyses reported in the technical literature must be regarded with skepticism.

The present free world production of rhenium is probably only a few hundred pounds per year. However, this could be increased rather quickly to at least several tons per year if the higher production level were warranted by increased demand for the metal. In addition, the deposits at Mansfeld in East Germany are still being worked and there is some production from U.S.S.R. sources. However, little authoritative information is available on such rhenium production.

Rhenium is believed to be potentially available in the United States at a rate of five or more tons per year as a by-product in the recovery of molybdenum from porphyry copper deposits. This will probably be the chief commercial source in this country in the immediate future, although some other sources are a possibility for future development.

In recent years and at present, production of rhenium and rhenium compounds in the U.S.A. has been limited by the demand to only a small fraction of the available supply. For many years the only source of rhenium compounds was the University of Tennessee. Rhenium was recovered there from flue dust obtained in roasting molybdenite from copper ores of the Miami Copper Company of Miami, Arizona. Flue dust processed at the University of Tennessee have contained from 0.3 to 1.5 per cent rhenium, but material now being processed is believed to be much less than 0.3 per cent. Although it has been stated that the production from this source could be increased if the demand warranted, production to date has been on a very limited scale, and is currently of the order of 50 pounds per year.

For several years the Kennecott Copper Company has recovered rhenium salts as a by-product of its molybdenum operations, which in turn is a by-product from their copper concentrating plants. Rhenium powder and fabricated rhenium are currently produced by the Chase Brass and Copper Company, a Kennecott subsidiary.

A rhenium deposit has recently been found at the Sun Valley Mine in Coconino County, Arizona. The rhenium is associated with uranium and molybdenum, prin-

References p. 191

ipally as a soluble oxide. The rhenium content varies from 0.01 to 0.1 per cent making this a relatively rich deposit although possibly not one that is extensive.

Rhenium powder prepared by hydrogen reduction of ammonium perrhenate sells or approximately $ 550 to $ 700 per pound, and sintered bars sell for about $ 800 per pound. Rod, wire, and and sheet are available in pound lots at prices from $ 900 o $ 2,000 per pound, depending upon the sizes and quantity ordered.

EXTRACTION

Numerous methods have been used for the separation, concentration, and recovery of rhenium salts and rhenium metal. However, most of these processes are too complicated for industrial application and will not be discussed.

The various methods developed for the recovery of rhenium depend on one or more of the following significant properties of rhenium compounds:

(1) The insolubility of rhenium sulfides in aqueous solution.
(2) The volatility of rhenium heptoxide.
(3) The solubility of rhenium heptoxide in water.
(4) The relative insolubility of potassium perrhenate in water.
(5) The temperature dependence of the solubility of potassium perrhenate in water.

The Feit process

The process used for the production of rhenium from the complex sulfide slimes obtained from the Mansfeld deposits is known as the FEIT process[5]. In the FEIT process the sulfide slime is extracted with water. Copper, nickel and zinc are precipitated as the double ammonium sulfates on the addition of ammonium sulfate. After removal of the copper, nickel and zinc double sulfates, additional ammonium sulfate is added to precipitate molybdenum, vanadium and phosphorus as complex oxides. After filtration, potassium chloride is added to the filtrate to precipitate crude potassium perrhenate, which is purified by recrystallization.

University of Tennessee process

Rhenium is recovered[6] at the University of Tennessee from flue dusts containing rhenium oxides. The rhenium heptoxide is removed from the concentrate by leaching with water, and is subsequently recovered from the leach solution by precipitation as potassium perrhenate on the addition of potassium chloride. The potassium perrhenate is then purified by recrystallization from aqueous solution.

Other processes

Rhenium is recovered as potassium perrhenate or ammonium perrhenate by the Kennecott Copper Corporation, but details of the Kennecott process have not been published.

Numerous extractive processes have been tried on a laboratory scale. Most of these involve separations based on the properties previously outlined. One process which represents a distinct departure from the others used to date involves the recovery of rhenium by ion exchange. There is no indication as yet that ion exchange is of commercial interest, but the process has been carried out successfully on a laboratory scale and may find commercial application in the future.

References p. 191

PRODUCTION OF RHENIUM METAL

Rhenium metal can be prepared by hydrogen reduction of the oxides, the sulfides, the halides or the perrhenates, but is most commonly prepared by hydrogen reduction of either potassium perrhenate or ammonium perrhenate. Potassium perrhenate is frequently used because it is available commercially, but a purer product is obtained if ammonium perrhenate is used as the source of rhenium.

Potassium perrhenate is readily reduced by hydrogen at 550°C to yield rhenium metal contaminated with potassium hydroxide. On washing the product with water, the potassium content can be reduced to about 0.4 per cent, but even repeated washings will not give complete removal of potassium.

Since the residual potassium hydroxide prevents satisfactory consolidation of the metal by powder-metallurgy methods, hydrogen reduction of the potassium perrhenate is not considered to be a satisfactory method of producing rhenium powder for powder-metallurgy work.

However, the potassium perrhenate can be converted to ammonium perrhenate which can, in turn, be reduced with hydrogen to yield a purer grade of rhenium powder.

In early work at Battelle[7], crude rhenium metal, obtained by hydrogen reduction of potassium perrhenate, was oxidized to form rhenium heptoxide which was sublimed and then condensed as a dense solid, substantially free of potassium hydroxide, the potassium hydroxide remaining in the nonvolatile residue. The heptoxide was dissolved in water and ammonium perrhenate was precipitated on the addition of ammonium hydroxide.

Although hydrogen reduction of ammonium perrhenate, prepared in this manner, initially gave rhenium powder of satisfactory purity, it was found that, when residues were reprocessed, small amounts of potassium appeared in the powder from time to time.

Therefore, an alternate method was developed which permitted more effective removal of the potassium.

In this method, which has been referred to as the "hydrolysis" method[7], the crude metal was chlorinated at 750–850°C, and the resultant pentachloride was reacted with water to form hydrated rhenium dioxide. The dioxide was filtered and then reduced with hydrogen at 600–800°C to yield minus-250-mesh rhenium powder.

Rhenium metal prepared by this method has been of consistently high purity, *i.e.*, 99.95 per cent. The particle size of metal powder prepared by the hydrolysis method is such that the material can be processed directly by standard powder-metallurgy techniques.

In typical processing schedules, rhenium is pressed at 30 tons per square inch, presintered by heating at 1200°C in a good vacuum for two hours, and sintered at 2700°C for one hour in hydrogen. Rhenium is hot-short and is, therefore, cold worked[8,9]. Some care is required in the initial "breakdown" of sintered powder-metallurgy bars which are subject to transverse cracking. Light reductions in cross-sectional area (one to three per cent) are made until about 10 per cent total reduction has been attained. Intermediate half-hour anneals in hydrogen at 1700–1800°C are required to offset the rapid work-hardening characteristics of the metal. Subsequent cold reductions of 10 to 20 per cent are then possible, but annealing time in the

References p. 191

TABLE I. PROPERTIES OF RHENIUM

Property	Value
Physical	
Density, at 20°C, g/cm³	21.02±0.01
Lattice constants (hexagonal close-packed structure), Ångstroms	$a_0 = 2.760 \pm 0.001$
	$c_0 = 4.458 \pm 0.005$
c/a ratio	1.615
Melting point, °C	3180±20
Boiling point (estimated), °C	5630
Vapor pressure at 2250°C, mm Hg × 10^{-6}	1.98
at 2725°C, mm Hg × 10^{-4}	5.60
at m.p. (estimated), mm Hg × 10^{-2}	2.77
Specific heat at 0°C, cal/degree/mole	6.07
at 2725°C, cal/degree/mole	9.43
Thermal expansion, β (001), cgs units × 10^{-6}	12.45±8%
β (100), cgs units × 10^{-6}	4.67±8%
Coefficient of linear thermal expansion, 20–1000°C, per °C × 10^{-6}	6.8
Thermal emissivity, $E\lambda$, at 1400°C	0.425
at 2800°C	0.366
Superconducting transition temperature, T_c, °K	1.699±0.001
Debye temperature, Θ, °K	294
Electrical resistivity, ϱ, at 20°C, microhm/cm	19
at 925°C, microhm/cm	78
at 1225°C, microhm/cm	90
at 1725°C, microhm/cm	107
Temperature coefficient of resistivity at 20°C, per °C × 10^{-3}	3.1
Thermionic work function, electron volts	4.80
Richardson constant, A, amperes/°K²cm²	52
Mechanical	
Modulus of elasticity (annealed rod) at 0°C, psi × 10^6	66.7±2.9
at 880°C, psi × 10^6	54
Ultimate tensile strength,	
annealed rod at room temperature, psi	164,000
annealed 5 mil sheet at room temperature, psi	150,000
10% cold rolled 5 mil sheet at room temperature, psi	272,000
15% cold reduced (swaged) 0.05–0.065 inch dia. wire at room temperature, psi	335,000
20% cold rolled 5 mil sheet at room temperature, psi	287,000
0.2% Offset yield strength,	
annealed rod at room temperature, psi	46,000
annealed 5 mil sheet at room temperature, psi	39,000
10% cold rolled 5 mil sheet at room temperature, psi	255,000
20% cold rolled 5 mil sheet at room temperature, psi	274,000
Proportional limit,	
annealed rod at room temperature (standard 1/8 inch diameter reduced section, 1/2 inch gage length), psi	26,300
Elongation,	
annealed rod at room temperature, 1/2 inch gage length, %	24
annealed 5 mil sheet at room temperature, 3/8 inch reduced dia. section, 2 inch gage length, %	19
10% cold rolled 5 mil sheet at room temperature, 3/8 inch dia. reduced section, 2 inch gage length, %	3
20% cold rolled 5 mil sheet at room temperature, 3/8 inch dia. reduced section, 2 inch gage length, %	2
Reduction in area,	
annealed rod at room temperature, %	21.7
annealed 10.1 mil sheet at room temperature, %	30.0
Strain hardening exponent, n	
annealed rod	0.353
Hardness,	
annealed, swaged rod, Vickers No.	270
30% reduced, swaged rod, Vickers No.	820
Recrystallization temperature, 20% cold reduced rod, °C	1,300

1700–1800°C range must be increased to two hours so that the surface hardness of the metal can be reduced below 300 Vickers. Rhenium can be rolled to thin sheet or swaged satisfactorily and drawn to wire, but wire drawing is difficult.

PROPERTIES OF RHENIUM

Table I contains a summary of some of the more important physical and mechanical properties of rhenium. Outstanding are rhenium's high density, melting point, modulus of elasticity, and rate of work hardening. Rhenium also has a relatively low vapor pressure (about $1\frac{1}{2}$ times that of tantalum). It is ductile at room temperature and is not made brittle by recrystallization. In spite of the fact that rhenium exhibits hot shortness if attempts are made to hot work it, high stress-rupture properties are obtained at elevated temperatures if tested in a reducing atmosphere.

Rhenium forms volatile oxides rapidly at temperatures above 550°C and, hence, must be protected against oxidation at elevated temperatures. In addition to the oxides, many other compounds of rhenium are known, since it can possess valence states from $^{-1}$ to $^{+7}$. The more important compounds are perrhenic acid, ammonium perrhenate, potassium perrhenate, the fluorides, the chlorides, the bromides and the sulfides. Rhenium apparently does not form stable carbides, is virtually inert to attack by iodine and by most iodides and is resistant to attack by molten tin, zinc, silver and copper[10,11]. It also is resistant to the so-called "water cycle"[12] which may occur in some high vacuum high-temperature devices. Rhenium forms extensive solid solutions with a number of other refractory metals.

APPLICATIONS

The scarcity and high cost of rhenium preclude its extensive use in large structural applications. However, rhenium is a potentially useful material in electronic tubes for such structures as heaters, grids and support wires. Its good room temperature ductility facilitates its use in such applications.

Rhenium–molybdenum alloys (approximately 50–50 composition) have been used in Europe for many years in wire form for tube parts, and increased use of these readily fabricable alloys is anticipated.

Cast rhenium alloys have been used in Europe for pen points. The high hardness of cold-worked rhenium, in the as-worked condition (in excess of 800 Vickers), may prove important in applications in which wear resistance is at a premium.

The fact that a conducting oxide film is formed on rhenium when used as an electrical contact, together with the resistance of rhenium to corrosion by marine atmospheres, have led to the use of rhenium as a contact material in marine magnetos.

The resistance of rhenium to water cycle attack has prompted its use as a projection lamp filament, in which application it has had an extended life.

The fact that rhenium coatings can readily be formed either by plating from an aqueous bath or from the vapor phase is also important in such applications as those where corrosion or wear resistance, or both, are required. Vapor phase methods can also be used to prepare massive metal of good quality.

Rhenium does not form stable carbides but does have an appreciable solubility in carbon. The rhenium–carbon eutectic melts at 2480°C. Rhenium is superior to tungsten at elevated temperatures in a carbonaceous atmosphere, but in direct contact with carbon this superiority would probably be less pronounced.

References p. 191

The thermoelectric power of rhenium[11] is such that it can be used in combination with platinum, molybdenum, or tungsten under nonoxidizing conditions at very high temperatures. Tungsten with tungsten–rhenium alloy makes a particularly promising thermocouple.

Thorium oxide additions markedly lower the work function of rhenium as well as of tungsten. Pure rhenium has a work function of 4.80 eV (at a Richardson constant of 52). Rhenium–2.28 per cent thoria (the optimum thoria content on the basis of present information) has a work function of 2.58 eV (at a Richardson constant of 1.4 $A/cm^{-2}/deg^{-2}$).

In the future, rhenium can be expected to occupy an important position among the minor metals in applications where its unique properties constitute a major advantage over those of other refractory metals.

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EQUILIBRIUM DIAGRAMS WITH InSb AS ONE COMPONENT

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(Received February 16th, 1959)

SUMMARY

The three equilibrium diagrams formed from InSb with tin, germanium, and GaSb respectively have been investigated by thermal, X-ray and metallographic techniques, and a diagram for each system is given. The InSb–Sn system shows a peritectic form with a peritectic line at 235°C. No solid solution of InSb in Sn is detected but the limit of solid solution at the tin end of the diagram is estimated to be 92 at. % Sn. The InSb–Ge system shows eutectic behaviour, with eutectic temperature of 512.5°C and eutectic composition 5 at. % Ge. No solid solution of InSb in germanium is detected but there is approximately 0.75 at. % solution of germanium in InSb. The InSb–GaSb system shows complete solid solution throughout the whole range of composition, but this result is only obtained after very long annealing. In both the InSb–Sn and InSb–Ge systems, there is evidence for the occurrence of a three-phase field, indicating that these diagrams can not be treated as quasi-binary.

1. INTRODUCTION

In recent years a knowledge of the equilibrium diagrams in which the compound InSb is one component has become of interest because of the possible importance in the production of semi-conducting devices. In the production of InSb for such applications, and in the use of such techniques as doping and zone melting etc., a knowledge of the relevant equilibrium diagram is necessary. The work described here is specifically concerned with the equilibrium diagrams of InSb with Ge, Sn and GaSb. Work has been carried out also on InSb–AlSb and InSb–InAs, but this is described elsewhere[1]. It has been generally assumed in much of the previous work that because of the properties of InSb such diagrams can be treated as quasi-binary, but our results show that such an assumption is not necessarily valid.

The InSb–Sn system

This system has been studied by BARUCH AND DESSE[2], who assumed quasi-binary behaviour, and suggested a eutectic diagram in which the eutectic composition was 66 at. % Sn, 17 at. % In, 17 at. % Sb, and the eutectic temperature 230 ± 2°C. Also they claimed less than 2% solubility of InSb in Sn and no observable solubility of Sn in InSb. In addition they observed a transition across the whole of the diagram at 212°C for which they could not account.

Since the measurements described here were completed, further results in this system have been published by ZITTER[3]. ZITTER obtains a peritectic diagram, the

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References p. 198

peritectic halt being at 235°C, and obtains solid solution of InSb in Sn up to approximately 92% Sn, but less than 0.5% solution of Sn in InSb. Again an unexplained arrest is obtained across the diagram at approximately 215°C.

InSb–Ge system

No full investigation of this system seems to have been reported. Semi-conductor work indicates a very limited range of terminal solid solution at either end of the diagram, *e.g.* the work of KOLM, KULIN AND AVERBACH[4] indicates less than 1% solubility of Ge in InSb. The binary systems Ge–In and Ge–Sb show very little solubility of the elements In and Sb themselves in Ge[5].

InSb–GaSb system

More work has been carried out in this system. KÖSTER AND THOMA[6] reported a degenerate eutectic diagram without appreciable terminal solid solution, but GORYUNOVA AND FEDOROVA[7], investigating only two compositions in the system, obtained single phase equilibrium after a considerable time of anneal at high temperatures. X-ray investigation by the present authors[8] showed that complete solid solution could be obtained at all compositions provided that the alloys were annealed in the powder form for a period of some eight weeks at temperatures comparable with the melting point of InSb. A preliminary report of the form of the equilibrium diagram for this system has already been published[1]. In a recent publication, KÖSTER AND ULRICH[9] confirm that their previous results were in error, and agree that solid solution occurs at all compositions.

2. GENERAL METHOD

The InSb to be used in the work was prepared from the elements by sealing the required quantities in an evacuated silica tube, heating to a temperature between 700 and 800°C and allowing to cool. To ensure purity and homogeneity, the ingot was then zone-refined by the normal techniques. The alloys used in all of the investigations were made by placing the required quantities of InSb and the appropriate element in a silica crucible in a silica tube. This was evacuated and then swept through with a mixture of 90% nitrogen–10% hydrogen which had previously been passed through alkaline pyrogallol, Feiser's solution and a drying bottle of calcium chloride. The alloys were melted in a R.F. induction furnace and then cast in a side arm by tilting the tube. This enabled ingots to be produced in a form suitable for thermal measurements. In all cases, the elements used were of purity greater than 99.9%. The heat treatment of the various alloys will be considered in separate paragraphs.

When all measurements had been completed, specimen alloys from each diagram were sent to Messrs. Johnson Matthey for chemical analysis. In no case did the final composition vary by more than 1% from the initial weighed-out composition.

In the thermal measurements both normal cooling and heating techniques and also differential methods were used. In the latter, germanium was used as a standard substance in most cases, and copper filings were used at the tin-rich end of the InSb–Sn system. The results obtained by the two methods were found to be consistent. The furnace used was made from 'Kanthal' wire wound on a Mullite tube

References p. 198

some 75 cm long and 4.3 cm diameter, and well insulated, so that the temperature gradient in the working region was negligible. The current to the furnace was controlled by a 'Variac' transformer and a rheostat.

The alloys were contained in silica crucibles. In the normal methods, the crucible was approximately 1.2 cm diameter, and the volume of ingot was about 2.7 c.c. to give a depth of about 3.5 cm. In the differential method, smaller crucibles about 5 mm internal diameter were used, the volume of the ingot being about 1.8 c.c. which again gave a depth of about 3.5 cm. The stirrer and the thermocouple sheath were also made from suitable silica tubing. The whole system in the furnace was kept in a stream of nitrogen-hydrogen mixture mentioned above. In all cases, cooling rates of about 1°C/min were used.

The temperatures were measured by platinum–platinum 13% rhodium thermocouples. These were calibrated in the apparatus against the melting points of pure tin, lead, antimony, and the copper–silver eutectic (71.9 at. % Ag). The e.m.f. was measured to an accuracy of $\pm$ 2 μV by means of a standard potentiometer. In the differential method, the difference in e.m.f's was measured by a short period galvanometer used critically damped. The estimated average accuracy for the temperature determinations was $\pm$ 5° over parts of the liquidus and $\pm$ 2° for other lines in both the InSb–Sn and InSb–Ge systems and $\pm$ 5°C in the InSb–GaSb system.

3. LATTICE PARAMETER DETERMINATION FOR PURE InSb

In the determination of equilibrium diagrams, useful data on the range of terminal solid solution is frequently obtained by X-ray methods, and these methods have been used in the systems InSb–Sn and InSb–Ge described below. In order to obtain satisfactory data in this way, it is necessary to have an accurate measurement of the lattice parameter of the component concerned, in addition to those of the various alloys. The figures for the lattice parameter of InSb given in the literature seem to vary to some extent. KOLM, KULIN AND AVERBACH[4] used X-ray techniques to investigate the solid solution of small amounts of Si, Ge, Sn and Pb in InSb, and their figure for the InSb parameter is 6.4867 Å. In the present work, however, measurements of the InSb parameter with material of very good semi-conductor purity have been carried out using a 19-cm powder camera and Cu Kα radiation, and a value of 6.4794 $\pm$ 0.0003 Å has been obtained. This is in reasonable agreement with the results of GIESECKE AND PFISTER[10] who quote a value of 6.47877 $\pm$ 0.00005 Å for InSb. In a recent report, however, KOLM[14] quotes a value of 6.4780 Å as the value for InSb, so that possibly the earlier figure has been corrected.

4. RESULTS

InSb–Sn system

The liquidus points were obtained by cooling-curve measurements, using both the normal and differential methods, the ingots being prepared as described in § 2. Measurements of the solidus points were made by heating-curve methods on various alloys, some of which were first annealed to equilibrium at a temperature of approximately 200°C, and some chill-cast. Suitable alloys were annealed for approximately two weeks and then used for heating-curve measurements, both normal and differential. Under these conditions, consistent results were obtained.

References p. 198

The results are shown in Fig. 1. A peritectic line is obtained at 235°C in agreement with the results of ZITTER. A discontinuity at 213°C is obtained, which at tin percentages greater than 80 at. % slopes up to the tin melting point. In an attempt to determine the range of terminal solid solution at the InSb end of the diagram, X-ray techniques were used and X-ray powder photographs taken of annealed specimens. No appreciable change in lattice parameter could be observed, however, the lattice parameter for alloys containing 0.5, 0.75 and 1 at. % Sn respectively having, within the limits of experimental error, the same value as that quoted in § 3 for InSb. Annealed ingots were investigated by microscopic methods, both unetched and also etched with Vilella's reagent. From this work it was concluded that the range of solid solution at the InSb-rich end of the diagram is less than 0.5 at. % Sn, while at the tin-rich end, the limit of solid solution occurs at approximately 92 at. % Sn, the 94 at. % alloy being definitely single phase and the 90 at. % alloy being definitely two phase. This result, shown dotted in Fig. 1, is in agreement with the results of ZITTER and also of GOULDING[11].

In order to investigate further the region between 213°C and 235°C, an ingot containing 20 at. % Sn, after being annealed for two weeks at 200°C to bring to equilibrium, was heated up to 225°C under argon on a hot-stage microscope. Above 220°C definite signs of melting were observed although the temperature did not exceed 225°C. It is considered that this presence of a liquid phase below 235°C indicates ternary behaviour, this field being a three-phase field. Thus the InSb–Sn section

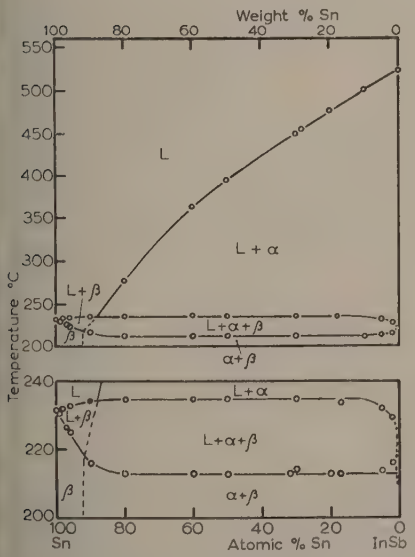

Fig. 1. Equilibrium diagram of InSb–Sn system.

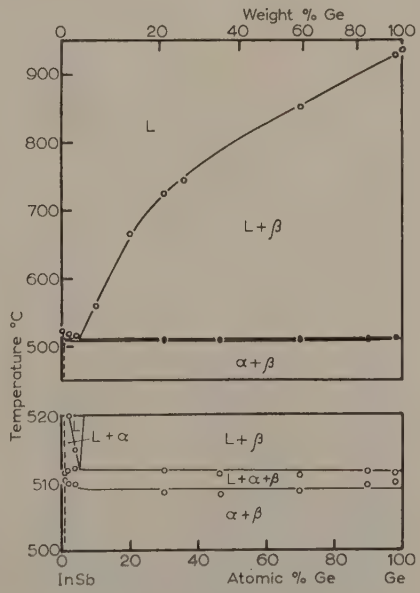

Fig. 2. Equilibrium diagram of InSb–Ge system.

References p. 198

is merely a general section of the In–Sb–Sn diagram and not a quasi-binary section. Fig. 1 has been drawn in this way. No boundary between the (L + α) and (L + α + β) fields could be detected, but this would probably be very difficult to detect. A dotted line is included in Fig. 1 to indicate this boundary.

InSb–Ge system

The methods used in this case were very similar to those described in the previous paragraph, but no differential measurements were made in this case. Again the results seem to indicate a general section of a ternary diagram containing a three-phase field, rather than the quasi-binary behaviour previously assumed. The diagram obtained is shown in Fig. 2. In this case, however, the diagram shows eutectic form, the eutectic composition being 5 at. % Ge and the eutectic temperature 512.5°C. In this case, the temperature range of the three-phase field is small (4°C maximum) and so hot-stage microscope work could not be carried out conclusively. The heating curve results, however, show the general form of the three-phase field.

Again it would appear that there is little terminal solid solution, and this was checked by X-ray measurements on annealed alloys. At the germanium-rich end of the section, a lattice parameter of 5.6570 ± 0.003 Å was obtained for Ge, and no difference in parameter could be detected for alloys containing 99, 99.25, and 99.5 at. % Ge respectively. At the InSb-rich end of the section, however, a variation in lattice parameter could be detected and the results are shown in Fig. 3. It is seen that this would indicate a limit of solid solution of about 0.75 at. % Ge in InSb.

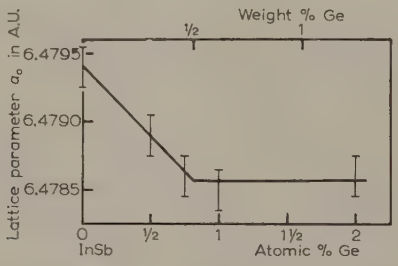

Fig. 3. Variation of lattice parameter a_0 as a function of percentage Ge in InSb–Ge alloys.

Although the results of KOLM, KULIN AND AVERBACH[4] are somewhat vitiated by the large value quoted for the InSb parameter, the parameter values quoted by them for alloys containing 1, 2 and 5 at. % Ge respectively are consistent with this suggested limit of solid solution.

InSb–GaSb system

The liquidus curve was determined as described above using alloys prepared as in § 2. The determination of the solidus was complicated by the great difficulty of obtaining alloys in equilibrium in the solid form. As has been previously reported[8], solid solution occurs at all compositions, but to obtain this equilibrium condition, alloys in

References p. 198

the powdered form must be annealed at temperatures close to the solidus for two to three months, while solid ingots may not reach equilibrium after annealing for a year. Since initially the solidus temperature is not known, the annealing to equilibrium is a tedious trial and error process. Even with the best conditions and three months' annealing, the high-angle lines in the X-ray photographs are still rather blurred, showing that complete homogeneity has not been obtained.

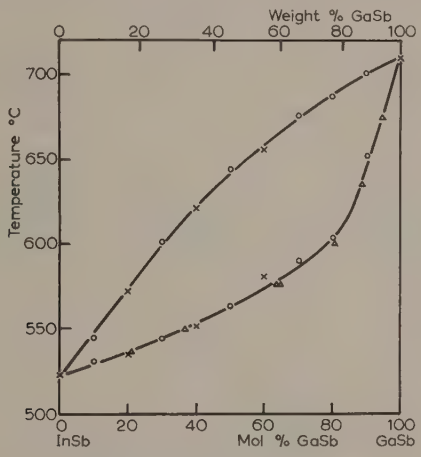

Fig. 4. Equilibrium diagram of InSb–GaSb system.
× ordinary thermal analysis
o differential thermal analysis
Δ X-ray measurements.

Alloys were treated in this way to produce the best degree of homogeneity available, and then were used for heating curves to determine the solidus points. Although in occasional cases, the degree of non-homogeneity caused the heating curves arrest to be somewhat indeterminate, a consistent set of results was obtained, and these are shown in Fig. 4, where points from both the normal heating methods and differential methods are plotted. Because of the very slow diffusion rates in these solids, an X-ray method of determining the solidus curve was also carried out, and this has already been described[1]. The results, plotted in Fig. 4, are seen to be in good agreement with the thermal results.

5. CONCLUSIONS

It has been suggested that because of the similarity of crystal structure of InSb with the other $A^{III}B^{V}$ compounds such as GaSb and with Ge and grey tin, considerable solid solution might occur. This could enable the production of alloys in which the important physical parameters could be steadily modified by suitable change of composition. Only the third system described here (InSb–GaSb) shows an extended range of solid solution. This is typical of a number of combinations of $A^{III}B^{V}$ compounds, and further work on the variation of physical properties with composition is being instigated.

References p. 198

In the systems InSb–Ge and InSb–Sn, little solid solution occurs, but the elements Ge and Sn can still be considered for doping in the semi-conductor applications of InSb. An important point about the diagrams obtained is the fact that ternary behaviour occurs. Similar behaviour has been observed in other systems involving $A^{III}B^{V}$ and $A_2^{III}B_3^{VI}$ compounds as one of the components[12,13]. When the section does not possess quasi-binary properties, the use of such techniques as zone refining etc. may be much more complicated.

ACKNOWLEDGEMENTS

The authors are indebted to Professor L. F. BATES for the facilities of his laboratory. The work described forms part of an investigation carried out for the Admiralty.

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EQUILIBRIUM DIAGRAM OF THE Ga_2Te_3-In_2Te_3 SYSTEM

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(Received February 16th, 1959)

SUMMARY

The equilibrium diagram for the Ga_2Te_3–In_2Te_3 system has been investigated by thermal and X-ray techniques, and a diagram is given. It is found that complete solid solution occurs throughout the whole range of composition, but the form of the liquidus and solidus curves show that the section is not quasi-binary and must be treated as a general section of the ternary system.

INTRODUCTION

In recent papers[1,2] various equilibrium diagrams involving $A^{III}B^{V}$ compounds have been discussed. It has been shown that in many cases where both components of the system are $A^{III}B^{V}$ compounds, solid solution occurs throughout the whole composition range. Owing to the very slow diffusion rates in these materials, it is possible to determine the solidus curve by X-ray techniques and in the case of GaSb–InSb, the X-ray results were checked against those for normal thermal methods and good agreement obtained. It has also been shown that the various diagrams concerned are quasi-binary in character. In the systems involving InSb as one component and either germanium or tin as the other, it has been shown that only very limited terminal solid solution occurs. Also it is found that these diagrams are not quasi-binary in character, and must be treated as a general section of a ternary system.

It has also been shown[3] that solid solution occurs throughout the whole composition range in certain systems involving $A_2^{III}B_3^{VI}$ compounds with zinc blende structure, *e.g.* Ga_2Te_3-In_2Te_3. While this work was being carried out, it was of interest to investigate the form of the equilibrium diagram for the Ga_2Te–In_2Te_3 system.

METHOD

Initially, to determine the solidus, the X-ray method as used for the mixed $A^{III}B^{V}$ systems was tried. But owing to the much greater diffusion rates in the present alloys as compared with $A^{III}B^{V}$ alloys, it was impossible to quench in the solid phase corresponding to equilibrium in the liquid-solid field. The investigation was therefore carried out by thermal methods. The techniques and apparatus were the same as for the GaSb–InSb work[2] and so will be mentioned only briefly here.

The compounds Ga_2Te_3 and In_2Te_3 were prepared from the elements by sealing

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References p. 201

appropriate quantities of these in an evacuated silica tube, heating to about 900°C and then quenching. Each of the alloys investigated was made from the compounds in a similar way, but in this case R.F. heating was used and the silica tube was filled with argon. The ingots were then used without further treatment for cooling curve measurements to determine the liquidus curve. For heating curve work, suitable ingots were first annealed at approximately 600°C for about two weeks before measurements were made. In all cases, the differential method of measurement was used, germanium being the standard substance, and a cooling (or heating) rate of approximately 1°C/min being used.

In all alloys, the indium and gallium used were of greater than 99.9% purity, but various grades of tellurium were used. In the initial measurements, normal commercial tellurium was used, but for more accurate measurements this was zone-refined to give high purity, and some tellurium of greater than 99.99% purity, obtained commercially, was also used. The main difference between the initial alloys and those using high purity tellurium was that the former gave less definite arrests. Alloys of the same composition held for different lengths of time at temperatures a little below the solidus, gave results in good agreement, indicating that there could be little loss of tellurium by dissociation.

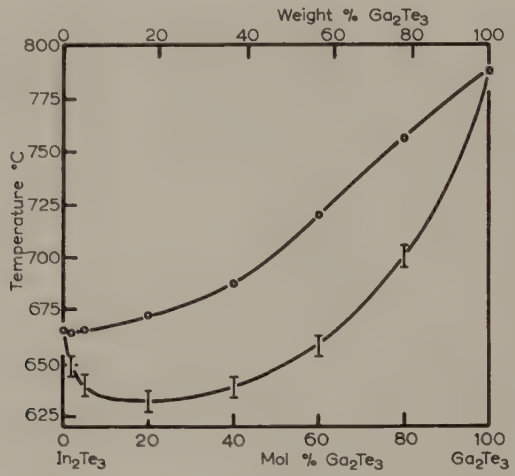

Fig. 1. Equilibrium diagram of Ga_2Te_3–In_2Te_3 system.

When the measurements were complete, as in the case of the InSb alloys, specimen alloys were sent to Messrs. Johnson Matthey for chemical analysis. The discrepancy between the final composition and initial weighed-out composition was less than 1%.

RESULTS

The results for the liquidus and solidus curves are shown in the figure. The relative accuracy of the liquidus points is estimated as ±3°C, while owing to the less definite

References p. 201

nature of the solidus arrests, the relative accuracy in this case is estimated as ± 5°C. The absolute accuracy of the points can be somewhat less than this, although the values for Ga_2Te_3 and In_2Te_3 are in good agreement with previous values[4].

To check the form of the solidus curve, alloys containing 20 mole % and 40 mole % Ga_2Te_3 respectively were heated to 650°C. When solid ingots were used, on quenching and X-raying, only single phase solid was obtained, due to the relatively rapid diffusion rates, and thus no indication of melting was obtained. When powdered alloys were heated to 650°C and then cooled, it was observed that melting had occurred.

Previous X-ray investigations[3] showed no signs of ordering occurring at any composition, nor any sign of a miscibility gap at lower temperatures.

CONCLUSIONS

It is clear from the form of the liquidus and solidus curves that this section does not show quasi-binary behaviour, a result which has already been shown to be the case for other sections involving $A_2^{III}B_3^{VI}$ compounds.

Some doubt as to the validity of these results may arise from the fact that the compounds concerned are said to be somewhat unstable and that the composition of Ga_2Te_3 in particular is relatively sensitive to the ambient tellurium vapour pressure. It was found however that repeated cooling runs on the same ingot gave consistent liquidus temperatures, and, as pointed out above, the solidus temperature seemed independent of the time the ingot was held in the apparatus. In addition, the Ga_2Te_3 specimen after measurements gave on chemical analysis the correct Ga to Te ratio within the limits of experimental error, and gave a satisfactory zinc blende structure on X-raying.

The fact that quasi-binary behaviour does not occur in such sections, in addition to the possible non-stoichiometry of the compounds mentioned above, means that the application of standard physical techniques for purification, *e.g.* zone refining and directional freezing, may not be possible for these compounds. This problem is being investigated further.

ACKNOWLEDGEMENTS

The authors are indebted to Professor L. F. BATES for the facilities of his laboratory. The work described forms part of an investigation carried out for the Admiralty.

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A STUDY OF RHODIUM(III) PERCHLORATE BY PAPER ELECTROPHORESIS AND SPECTROPHOTOMETRY

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SUMMARY

Evidence is presented that reaction of boiling sodium chlororhodite with 5 *M* $HClO_4$ does not produce a solution of pure $Rh(H_2O)_6^{3+}$. A method for the preparation of solid $Rh(H_2O)_6(ClO_4)_3$ is suggested. The absorption spectrum of its solution, its stability to heating and its electrophoretic properties were observed.

INTRODUCTION

A survey of the literature on rhodium(III) perchlorate revealed that apart from a few studies on the action of perchloric acid on some compounds of rhodium, no systematic study of this compound has been carried out, nor has it been prepared in the solid state.

GRUBE *et al.*[1,2] observed that when rhodium hydroxide reacts with $HClO_4$, a red solution is produced, which they claim contains $Rh(OH)_2ClO_4$. A basic perchlorate was also prepared by JØRGENSEN[3] by titrating 0.01 *M* Rh(III) with NaOH and $HClO_4$. The same author suggests a preparation of a rhodium perchlorate solution by boiling a solution of $Na_3RhCl_6 \cdot 12H_2O$ for half an hour with 5 *M* $HClO_4$ and dilution to 1 *M* $HClO_4$. This solution then gave a spectrum with two crystal field bands at 393 and about 305 mμ which were attributed to the ion $Rh(H_2O)_6^{3+}$.

Previous paper electrophoretic work from this laboratory[4-6] has shown that the removal of coordinated chloro-groups from the rhodium chloro-salts is not complete in one precipitation as hydroxide. A possible method for preparing the solution of only $Rh(H_2O)_6^{3+}$ was suggested by repeated precipitation with NaOH and dissolution in $HClO_4$. This treatment produces a single fast electrophoretic band. The polyhydroxy-compound observed in HCl, HNO_3, and HBr was not present in such solution.

In this paper we shall describe paper electrophoretic studies on solutions of rhodium perchlorate prepared by different methods, as well as the preparation and the properties solid rhodium perchlorate.

EXPERIMENTAL METHODS

Preparation of rhodium perchlorate solution

As reported previously[6], a solution of rhodium perchlorate was prepared by precipitating rhodium hydroxide from aqueous solution of Na_2RhCl_5(Johnson, Matthey

References p. 205

& Co.) with a slight excess of NaOH, dissolving the precipitate in $HClO_4$, and reprecipitating till the solution yielded a single fast band on electrophoresis in N $HClO_4$.

Paper electrophoresis

The glass plate technique was used (as described by LEDERER AND WARD[7]) with 250 V for 45 min, with paper strips 3 × 40 cm (Papier d'Arches No. 302) and N $HClO_4$ as electrolyte. For preparative purposes Whatman No. 3 MM papers were used. Detection of the bands was carried out by spraying with a mixture of $SnCl_2$ and KI in 5 N HCl and heating under an infra red lamp.

Spectrophotometry

Absorption spectra of solutions were measured with a spectrophotometer by Jobin & Yvon (Paris) in the region 250 to 550 mμ.

RESULTS AND DISCUSSION

Studies with the rhodium perchlorate prepared by boiling the chloro-salt with perchloric acid[3]

Sodium chlororhodite was boiled in 5 N $HClO_4$ as described by JØRGENSEN[3] and diluted to 1 M $HClO_4$. The absorption spectrum of our solution (Fig. 2–1) is identical

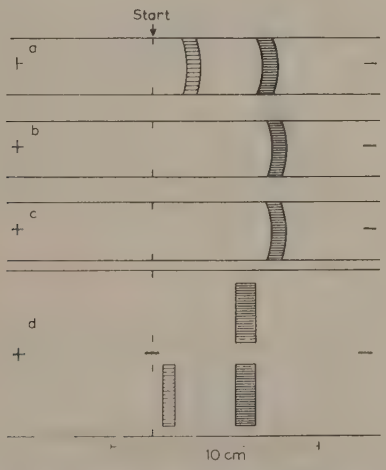

Fig. 1. Electropherograms of the solutions of rhodium perchlorate.
Conditions: 250 V for 45 min, electrolyte M $HClO_4$.
a) Solution of rhodium perchlorate prepared according to JØRGENSEN[3].
b) Solution of rhodium perchlorate prepared by reprecipitation according to SHUKLA[6].
c) Solution of rhodium perchlorate crystals.
d) Electrophorised on the same paper:
above, solution of rhodium perchlorate crystals;
below, solution of rhodium perchlorate prepared according to JØRGENSEN[3].

References p. 205

with that obtained by JØRGENSEN[3], with two prominent absorption maxima at 301 and 396 mμ (JØRGENSEN reporting 305 and 393 mμ).

When this solution is electrophorised with M $HClO_4$, two distinct cationic bands separate as shown in Fig. 1a, the faster one being more intense than the slower one. The faster band corresponds in speed to the rhodium perchlorate band found after repeated precipitation[6], while the slower one may or may not correspond to one of the slower bands found in the impure rhodium perchlorate[6].

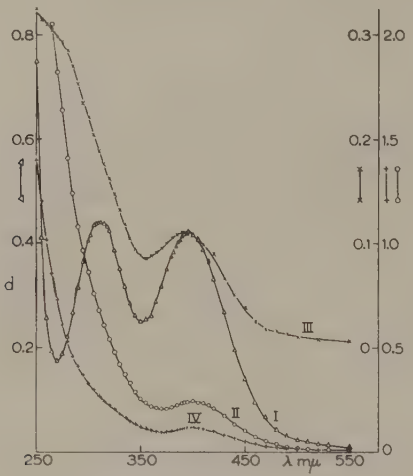

Fig. 2. Absorption curves of:

(I) Solution of rhodium perchlorate prepared according to JØRGENSEN[3].
(II) Solution of rhodium perchlorate prepared by reprecipitation according to SHUKLA[6].
(III) Solution obtained by eluting the most intense and fastest cationic electrophoretic band of the solution (I).
(IV) Solution of rhodium perchlorate crystals.

The faster band was eluted from the electropherogram and yielded the spectrum shown in Fig. 2–III, *i.e.* with a single absorption maximum at about 396 mμ. The absorption band at 305 mμ had disappeared.

This fast band has, however, the same absorption spectrum as a solution of rhodium perchlorate prepared by reprecipitation to electrophoretic homogeneity. Unfortunately the second electrophoretic band is present in such small amounts that numerous efforts to isolate sufficient for spectrophotometry have failed. The similarity of the spectra of the faster moving constituent and our rhodium perchlorate suggests strongly that the maximum at 301 mμ is due to the slower moving band.

We have also followed by paper electrophoresis the time of boiling necessary for obtaining a stable solution by reaction of $HClO_4$ with chlororhodite. The two bands appear after 10 minutes boiling and do not change on further boiling.

References p. 205

Preparation and properties of solid rhodium perchlorate

A solution of rhodium perchlorate was prepared by reprecipitation as described previously[6]. This solution yields a single electrophoretic band (Fig. 1 b) and has an absorption spectrum shown in Fig. 2–II. When this solution is evaporated in a vacuum desiccator at room temperature, yellow flat needle-like crystals separate out. These crystals were dried between filter papers and were found so hygroscopic that they had to be stored in a desiccator over H_2SO_4. A solution of these crystals in 1 *M* $HClO_4$ shows the same electrophoretic band and the same absorption spectrum as the solution from which the crystals were obtained (Fig. 1-d and Fig. 2–IV); thus it may be considered that no change occurred during crystallisation. Heating of a solution on the water bath for 1 hour did not produce any detectable change either.

Analysis of the solid rhodium perchlorate

The solid rhodium perchlorate was analysed for rhodium by reduction with metallic zinc powder and weighing as metallic rhodium after drying at 160°. The rhodium content was found to be 19.70 and 19.89% (calculated from the formula $Rh(H_2O)_6(ClO_4)_3$, the value for rhodium is 19.74%).

The estimation of perchlorate as nitron perchlorate gave 58.76 and 58.22% in the solid compound. The value for perchlorate calculated from the above formula was 58.58%.

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THE OXYTRICHLORIDES AND OXYTRIBROMIDES OF NIOBIUM (COLUMBIUM)(V) AND TANTALUM(V)

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SUMMARY

A number of methods of formation of niobium and tantalum oxytrichlorides and oxytribromides have been investigated. $NbOCl_3$, $NbOBr_3$ and $TaOBr_3$ have all been obtained in a crystalline condition by the action of molecular oxygen on the heated pentahalide. Tantalum oxytrichloride, which is thermally the least stable of these compounds has been obtained, in a non-crystalline condition, by pyrolysis of the pentachloride–diethyl ether complex.

Niobium oxytrichloride and oxytribromide can be sublimed in a vacuum without decomposition: the tantalum compounds cannot.

All four oxytrihalides undergo decomposition into pentahalide and pentoxide on heating, the niobium compounds being more stable in this respect than the tantalum.

The vapour pressure of niobium oxytrichloride has been measured up to a temperature ($\sim$ 340°C) at which thermal decomposition affects the results.

References have appeared in the literature from time to time regarding some of these oxytrihalides but, except in the case of niobium oxychloride, with little information concerning their methods of formation, characterisation or properties. Nevertheless, they are of frequent occurrence during the preparation of the pentahalides if any oxygen-containing compound is present, even if this is only oxide dissolved in the metal.

The present paper is an account of a systematic investigation of a number of different methods of preparation of these compounds and of their thermal stabilities and other properties. With the exception of tantalum oxytrichloride they have all been prepared in a crystalline condition.

The action of moisture on anhydrous pentahalide undoubtedly leads to the formation of oxytrihalide, but the reaction is difficult to control and leads to products of indeterminate character. Other more promising methods of preparation were therefore examined. These included: thermal decomposition of the pentahalide–diethyl ether complexes, the action of halogen on a heated mixture of carbon and the pentoxide, the action of a mixture of carbon dioxide and halogen on the heated metal and the direct oxidation of the pentahalide by oxygen. Of these, the last named was found to be much the most convenient method of preparation for all except tantalum oxytrichloride.

References p. 216

Crystalline oxytrihalides can only be prepared within a limited range of temperature, which is smaller for the tantalum compounds than for the niobium. If the temperature is too low, either no reaction occurs or the product is non crystalline; if too high, disproportionation into pentahalide and pentoxide takes place.

NIOBIUM OXYTRICHLORIDE

This is much the most stable of all the four oxytrihalides at present under consideration.

DEVILLE AND TROOST, in 1867[1], reported that it was formed when niobium pentachloride vapour was passed over the heated pentoxide. The same authors incidentally found no reaction to occur under the same conditions between tantalum pentachloride and pentoxide.

DELAFONTAINE AND LINEBARGER[2] obtained a mixture of pentachloride and oxytrichloride by the action of carbon tetrachloride vapour on heated niobium pentoxide.

SÜE[3] obtained a mixture of oxytrichloride and pentachloride by the action of chlorine on a mixture of carbon and pentoxide at 300°C, though the products apparently were not separated. He also[4] heated samples of niobium pentachloride in oxygen for measured intervals of time at various temperatures and showed that whilst in the region of 300°C, oxytrichloride was formed, the sole product above 500°C, was the pentoxide.

SPITSYN AND PREOBRAZHENSKIĬ[5] reported that when hydrogen chloride reacted with niobium dioxide the product was oxytrichloride. KANZELMEYER, RYAN AND FREUND[6] prepared niobium oxytrichloride by direct chlorination of niobium pentoxide mixed with carbon and by the thermal decomposition of the compound reported as $NbOCl_3,2CsCl$ by WEINLAND AND STORZ[7]. We tried this method but found it to be inconvenient and expensive and possessing no advantages as a method of preparation over those to be described.

CHAIGNEAU[8], whilst studying the preparation of niobium and tantalum pentahalides by the action of aluminium trihalides on the pentoxides, found that with niobium pentoxide some oxytrichloride was also formed.

Experimental

Thermal decomposition of niobium pentachloride–diethyl ether complex

When a sample of the complex $NbCl_5,(C_2H_5)_2O$, prepared as previously described[9], was heated in a vacuum for $3\frac{1}{2}$ h at 90°C, a residue of nearly pure oxytrichloride was obtained. [Found: Nb, 43.6; Cl, 47.2. $NbOCl_3$ requires Nb, 43.2; Cl, 49.4.] The crystallisation of the product however was imperfect, the X-ray diffraction lines being very broad and diffuse. On heating *in vacuo* to 200°C, the whole of the oxytrichloride sublimed unchanged. As the sublimate was condensed on to a cool surface, however, the X-ray diffraction lines of the product were still very broad.

The action of chlorine on a mixture of carbon and niobium pentoxide

Mixtures of niobium pentoxide and sugar carbon in ratios (w/w) of 2:1, 1:1, and 1:2 were heated at 500°C in a pyrex tube in a stream of dry chlorine, the rate of flow being approximately the same in each case. In all experiments a sublimate consisting of a mixture of $NbCl_5$ and $NbOCl_3$ was obtained. These could easily be separated by

References p. 216

maintaining the condensation zone at 160°C when the more volatile $NbCl_5$ was carried forward. [Found: Nb, 42.8; Cl, 48.6. $NbOCl_3$ requires Nb, 43.2; Cl, 49.4.] The simultaneous formation of oxytrichloride and pentachloride by this reaction has also been observed by LIND AND INGLES[10], who used the reaction for the preparation of niobium pentachloride from the pentoxide. They noted that below 500°C the greater part of the product was $NbOCl_3$, whilst at temperatures between 500°C and 1000°C approximately equimolar mixtures of $NbCl_5$ and $NbOCl_3$ were obtained. This result is interesting since niobium oxytrichloride in a static system undergoes decomposition into pentoxide and pentachloride at temperatures well below 1000°C and its occurrence in such experiments is to be attributed to its removal from the hot zone by the flow of gas. We have, similarly, observed the formation of oxytrichloride in a flow system at temperatures above those at which it decomposes *in vacuo*.

The action of aluminium chloride on niobium pentoxide

Aluminium chloride (Al_2Cl_6) and niobium pentoxide were mixed in equimolar proportions and heated in sealed tubes at several temperatures. Heating at 240°C gave some crystalline oxytrichloride which disproportionated on further heating, whilst at 335°C the only product was the pentachloride. This reaction therefore is more suited to the preparation of the pentachloride (CHAIGNEAU) than of the oxytrichloride.

The reaction of molecular oxygen with niobium pentachloride

This was found to be the most convenient and successful method of preparation. A quantity of pure pentachloride was sublimed through a side arm into a 20 mm diam. reaction tube which contained a quantity of purified and dried glass wool to increase the surface of the pentachloride exposed to the oxygen. The tube was surrounded by a thermocouple-controlled heater and a slow stream (*ca.* 20 c.c./min) of dry oxygen passed over the pentachloride. The temperature was raised to 150°C at which the partial pressure of the pentachloride was about 11 mm[11], and in two hours about 80% of a charge of $\sim$ 2 g $NbCl_5$ was converted into oxytrichloride, 20% being carried forward into the cooled part of the reaction tube. By evacuating the tube and changing the position of the heater this could be sublimed back into the reaction tube and re-oxygenated, leading eventually to an almost 100% conversion into oxytrichloride. At the conclusion of the reaction the temperature was raised to 200°C and the oxytrichloride sublimed in a stream of oxygen into a further tube maintained at 100°C. On the surface of this tube the oxytrichloride condensed in the form of radiating rosettes of needle-like crystals, several mm in diameter.

This rosette-like habit is in sharp contrast to the usual appearance of niobium oxytrichloride, which condenses on to a cold surface as a feathery mat of extremely fine silky needles, or extends into the space of the tube as a tenuous gossamer veil.

SANDS, ZALKIN AND ELSON[12], who have recently examined the crystal structure of niobium oxytrichloride report that when prepared by the action of carbon tetrachloride on niobium pentoxide and distilled at 200°C from unreacted oxide it condenses to a hygroscopic product with a fibrous appearance resembling white "cotton-batting". They obtained crystals suitable for diffraction studies by heating this product in closed capillaries to about 350°C and slowly cooling.

References p. 216

They report that the compound, which crystallises in the tetragonal space group D_{4h}^{12}/mnm, forms "peculiar polymeric chains of $NbOCl_3$ dimers" formed from planar Nb_2Cl_6 groups, joined by Nb–O–Nb bonds into infinite chains parallel to the C axis. This tendency of niobium oxytrichloride towards a chain-like polymerisation is undoubtedly the cause of the formation of gossamer-like structures which we have often observed and which in turn lead to the great difficulty of separating niobium pentachloride from niobium oxytrichloride by a distillation process or rapid sublimation, even though the vapour pressure of the oxytrichloride is less than a twentieth of that of the pentachloride at the normal boiling point of the latter.

Niobium oxytrichloride is freely soluble in molten pentachloride. In one experiment 0.391 g $NbOCl_3$ dissolved in 1.105 g $NbCl_5$ to give a deep red liquid which solidified on cooling to a green solid. It has not yet been established whether or not oxytrichloride and pentachloride form mixed crystals.

AINSCOUGH, HOLT AND TROWSE[13] have stated that it is not possible to separate niobium oxytrichloride and pentachloride by vacuum sublimation at 200°C. They further claim that the difference between their estimation of the boiling point of niobium pentachloride and that of ALEXANDER AND FAIRBROTHER[11] may have been due to contamination by oxytrichloride, though a rise in b.p. of 7° of a solvent with latent heat of volatilisation of 13.2 kcal/mole would require an impossibly large contamination, and the same explanation would not account for a rise in the triple point of about 6°C. Moreover, a similar discrepancy between the boiling point estimations of tantalum pentachloride could not possibly have been due to the presence of tantalum oxytrichloride, for as is shown below, this is unstable at the boiling point of the pentachloride.

It should be added that the statement of AINSCOUGH, HOLT AND TROWSE, as part of this argument, that the temperature of sublimation used by ALEXANDER AND FAIRBROTHER was 200°C, is incorrect as it stands. The purification of niobium and tantalum pentachlorides was carried out slowly, through some 16 bulbs, much of it at a temperature well below 200°C.

In view of the frequent occurrence of niobium oxytrichloride in preparations of the pentachloride and the difficulty of separating the two compounds completely, it seemed very desirable to measure the vapour pressure of niobium oxytrichloride. That its vapour pressure is very much less than that of the pentachloride may easily be observed by the relative slowness with which it sublimes in an evacuated and sealed tube between 150°C and 200°C.

For example, a sample of oxytrichloride was heated for 11 h at $\sim 10^{-5}$ mm Hg, in an evacuated sublimation line at 132°C during which no sublimation was observed. During a further 30 min at 165°C a minute amount of sublimate formed, whilst at 210°C the sublimation was complete after 3 h, leaving no residue. An analysis of the sublimate gave: Nb, 43.4; Cl, 49.2. $NbOCl_3$ requires Nb, 43.2; Cl, 49.4.

The vapour pressure was measured by a static method, using a sensitive sickle gauge, in the same manner and with much of the same apparatus as used by ALEXANDER AND FAIRBROTHER[11] for the measurements of the vapour pressures of the pentachloride and pentabromide.

The results are given in Table I and shown in Fig. 1, on which also is shown a portion of the vapour pressure curve of niobium pentachloride.

Up to a temperature of about 330°C the pressure rose in a normal manner, the

References p. 216

log p - $1/T$ plot (Fig. 2) being reasonably linear and giving by the method of least squares a heat of sublimation of 23.3 kcal/mole.

From about 340°C upwards the rise of pressure with temperature became less steep, in the way that usually indicates liquefaction or a change of structure, and also became irreversible. When a specimen of $NbOCl_3$ was heated up to 400°C in a sealed evacuated

TABLE I

Temperature °C	*Pressure* mm
233.9	9.7
260.0	29.7
273.8	56.1
305.0	132.5
316.4	183.3
328.4	298.1
338.9	310.8
358.8	314.9
375.0	337.9
390.0	349.5

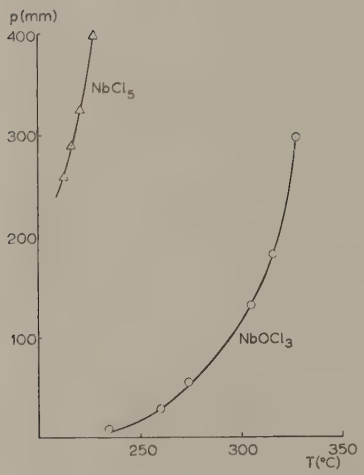

Fig. 1.

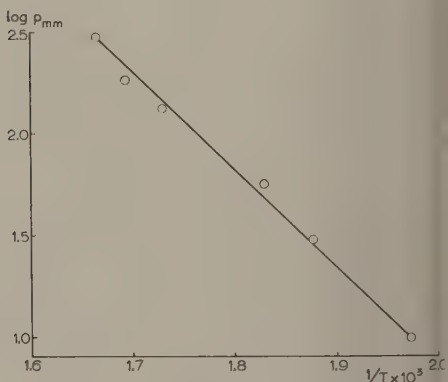

Fig. 2.

tube, however, no liquefaction occurred but a small amount of yellow pentachloride was produced, indicating that a disproportionation into pentachloride and pentoxide was taking place. It seems probable that below 400°C the rate of disproportionation is slow and only observed in these experiments because the temperature was maintained constant for at least an hour before each observation of the pressure.

Confirmation of the onset of disproportionation below 400°C was obtained by X-ray diffraction photographs of a specimen in a sealed quartz capillary tube, before and after heating to 360°C for 1 h. The latter photograph showed the presence of lines characteristic of Nb_2O_5.

References p. 216

The falling away and irreversibility of the vapour pressure above 350°C is to be attributed to non-saturation of the vapour phase. All experiments with this and other oxyhalides showed that even at temperatures well above those at which some disproportionation was observed, the sublimation of the pentahalide away from the residual pentoxide structure was usually very slow.

Both qualitative and quantitative observation therefore indicate that even at 200°C it should be possible to separate niobium pentachloride and oxytrichloride, but practice shows that this is only possible when carried out very slowly and repeated many times, the oxytrichloride otherwise being carried with the pentachloride as a dispersed solid phase.

Although niobium pentachloride is an effective catalyst in the acylation of toluene[14], experiments showed that in the same reaction the oxytrichloride is without any catalytic action.

The niobium oxytrichloride dissolved immediately and without residue in a 50/50 mixture of water and monoisopropylamine, from which niobic acid in an easily filtrable form was immediately precipitated on acidification with acetic acid.

TANTALUM OXYTRICHLORIDE

This proved to be the most elusive of the four oxytrihalides and much less stable than the corresponding niobium compound. This instability has been a common experience. DEVILLE AND TROOST found that even after passing pentachloride vapour eight times over tantalum pentoxide, no formation of oxychloride could be observed. RUFF AND THOMAS[15], who remarked that up to the time of writing no oxychloride of tantalum had been observed, stated that they had obtained a residue with the composition TaO_2Cl after subliming the pentachloride at 1–2 mm and 200°–220°C from the product of the action of carbon tetrachloride and chlorine on the pentoxide, and heating the residue to 500°C.

We also on one occasion obtained a residue with a similar analysis. Since, however, examination by X-ray diffraction of the thermal decomposition of the other three oxytrichlorides, all of which were obtained in a crystalline condition, gave no evidence of an intermediate product of a composition MO_2X, but only of the pentoxide and pentahalide, it seems probable that this composition was fortuitous. Moreover when a sample of tantalum pentachloride (b.p. 239°C) was heated in a sealed tube with tantalum pentoxide at 360°C for 12 h and the product examined by X-ray diffraction, no new crystalline product could be identified.

Experimental

The action of chlorine on a mixture of carbon and tantalum pentoxide

Passage of chlorine at 400°C over a 2:1 carbon–tantalum pentoxide mixture gave a white sublimate immediately outside the heated zone. When this was heated at 57°C in a vacuum, a sublimate of pentachloride and a residue mainly of pentachloride with a little pentoxide was obtained. The X-ray diffraction photograph of the residue included a single line in the same position as a strong line in the niobium oxytrichloride photograph. Since the crystalline niobium and tantalum oxytrihalides show considerable similarities in their X-ray diffraction patterns (Fig. 3), it seems possible that some tantalum oxytrichloride may have been formed and carried along with the

References p. 216

chlorine stream but that most of it was decomposed into the pentoxide and the pentachloride. This would account for the presence of oxide in the first sublimate and further suggests that oxytrichlorides of niobium and tantalum are formed as the primary products of chlorination in this method, rather than by a reaction between pentoxide and pentachloride. The easy disproportionation of tantalum oxytrichloride is in accord with other experiments.

The direct oxidation of tantalum pentachloride

This also proved ineffective as a method of preparation. Using the same apparatus as for the oxidation of niobium pentachloride, it was found that below 130°C no reaction occurred, and that when tantalum pentachloride was heated with oxygen for 48 h at 130°C the only solid product was the pentoxide. A shorter time of contact between the reactants at 190°C again showed traces in the X-ray diffraction photograph of a product which might have been an oxyhalide. As a preparative method however this reaction is clearly of no use.

Pyrolysis of tantalum pentachloride–diethyl ether complex

Colourless crystals of the complex prepared as previously described[9] were heated *in vacuo* at various temperatures and the products analysed. Pyrolysis occurred even at 65°C. By heating a sample for 17 h at this temperature a product with a composition close to $TaOCl_3$ was obtained. [Found: Ta, 60.1; Cl, 34.7; $TaOCl_3$ requires Ta, 59.7; Cl, 35.1.] Prolonged heating at 100–150°C gave clear evidence of a further elimination of chlorine from the product, and at 275°C a crystalline sublimate of tantalum pentachloride was obtained. After heating for 16 h at 490°C it was found that disproportionation of the oxytrichloride was complete and both chemical analysis and X-ray diffraction showed that only crystalline tantalum pentoxide was present in the residue.

The tantalum oxytrichloride was therefore only obtained as a white non-crystalline powder, which could not be sublimed *in vacuo* without decomposition.

NIOBIUM OXYTRIBROMIDE

Apart from an observation by Rose in 1858[16], of the formation of a voluminous yellow-coloured product, which he called "niobunterbromide" but did not analyse, by the action of bromine and carbon dioxide on a mixture of niobium pentoxide and carbon, the only reference to this compound appears to be in a paper by Barr[17], who was chiefly interested in the preparation of the pentabromide. Using the same reaction, but with nitrogen as a carrier gas, Barr also obtained a bright yellow very voluminous powder, which sublimed at the heat of the Bunsen flame without melting. It could be sublimed in an atmosphere of nitrogen or carbon dioxide containing bromine, but "even in this atmosphere" he detected a partial breakdown into pentoxide and pentabromide. The analysis corresponded closely to that of niobium oxytribromide. The compound has however not been prepared hitherto in a recognizable crystalline state.

Experimental

The action of bromine on a mixture of carbon and niobium pentoxide

A stream of nitrogen saturated at room temperature with bromine was passed

References p. 216

over a 2:1 carbon–niobium pentoxide mixture at 540°C. A yellow-orange sublimate was obtained. This was further subdivided by volatilisation *in vacuo*; at 130°C over 12 h no appreciable sublimation occurred, but at 167°C over 24 h, a considerable proportion volatilised. Both this and the residue of the initial product were analysed and found to consist essentially of $NbOBr_3$. [Residue: Nb, 27.8; Br, 68.2. Sublimate: Nb, 25.9; Br, 65.8. $NbOBr_3$ requires Nb, 26.6; Br, 68.8.] Likewise, X-ray diffraction photographs showed no trace of the easily identifiable niobium pentabromide. It was observed that after the rough fractionation at 167°C the residue was more coarsely crystalline than the sublimate.

Pyrolysis of niobium pentabromide–diethyl ether complex

The complex, prepared as already described[9], was heated in a vacuum for 6 h at 112°C when a brownish residue of $NbOBr_3$ remained. [Found: Nb, 26.7; Br, 67.0.] On heating *in vacuo* to 250°C the oxytribromide sublimed completely leaving no residue.

The action of oxygen on niobium pentabromide

This was carried out in a similar manner to that described for niobium oxytrichloride. The pentabromide was oxidised at 150°C where the reaction was rapid, 1 g pentabromide being oxidised within 1 h. At this temperature niobium pentabromide is solid and has a very low vapour pressure. Reaction would therefore appear to take place only on the surface of the solid. The product was sublimed *in vacuo* at 180°C and collected on a surface maintained at 90°C. The crystals appeared in the form of radiating rosettes very similar to those of niobium oxytrichloride collected in a similar manner.

Niobium oxytribromide is a yellow-brown crystalline solid which fumes on exposure to moist air. It is not a good Friedel-Crafts catalyst and, with toluene and acetyl chloride, only gives amounts of methyl acetophenone which are detectable by smell. It is, however, more reactive in this connection than niobium oxytrichloride.

Although no actual vapour-pressure measurements have been made, the comparative ease with which niobium oxytribromide can be sublimed *in vacuo* suggests that even at moderately low temperatures (< 200°C) it would be more difficult to separate from niobium pentabromide, which is the least volatile of the chlorides and bromides of these elements, than is niobium oxytrichloride from niobium pentachloride.

An examination of its thermal stability was carried out in the following manner. A quantity of re-sublimed oxytribromide was sealed into one end of an evacuated tube which was heated to a fixed temperature, the other end being cooled by a current of air. It was confirmed that sublimation occurred at 170°C without decomposition (X-ray analysis). A similar tube was wholly maintained for 1 h at each of a number of fixed temperatures, in steps of 10°, until signs of decomposition became evident. This was easily observed since the pentabromide is much darker in colour than the oxytribromide. Moreover, the pentabromide could be sublimed away from a residue which was whitish in appearance due to the formation of pentoxide. This decomposition first appeared, under these conditions, at 320°C at which the vapour pressure of niobium pentabromide is about 270 mm[11]. Niobium pentabromide could therefore

References p. 216

probably be freed from oxytribromide by maintaining it for some time at the boiling point (361.6°C) or by passing the vapour through a hot tube.

TANTALUM OXYTRIBROMIDE

This compound does not appear to have been previously described. It is thermally more stable than tantalum oxytrichloride and is correspondingly easier to prepare.

Experimental

The action of bromine on a mixture of carbon and tantalum pentoxide

A stream of nitrogen, saturated with bromine at room temperature was passed over a 2:1 mixture of carbon and tantalum pentoxide at 460°C. The reddish yellow sublimate gave: Ta, 32.9; Br, 65.9. $TaBr_5$ requires: Ta, 31.2; Br, 68.8. It is therefore evident that the product of this reaction was mainly tantalum pentabromide, the high tantalum and low bromine values indicating a small admixture of oxytribromide.

The reaction between tantalum pentabromide and tantalum pentoxide

When these two compounds were heated in stoichiometric proportions for 12 h at 360°C in a sealed tube (previously evacuated) and the contents examined by X-ray diffraction it was found that a very small amount of oxytribromide had been formed, the major proportion of the contents being unchanged. This is in contrast to the results of similar experiments with tantalum pentachloride in which no formation of oxytrichloride was observed.

Pyrolysis of tantalum pentabromide–diethyl ether complex

This was carried out by simply dissolving the pentabromide in excess of diethyl ether, removing the excess of ether and heating the product under vacuum. Two temperatures were used. Heating for a period of 29 h at 74°C resulted in a product which gave Ta, 41.5; Br, 52.4, and was therefore chiefly $TaOBr_3$. [Requires Ta, 41.4; Br, 54.9.] The product was microcrystalline with broad X-ray diffraction lines. The analyses of similar products which had been heated above 100°C showed evidence of a slow disproportionation into pentabromide and pentoxide.

The action of oxygen on tantalum pentabromide

Using the same apparatus as before, dry oxygen was passed over heated tantalum pentabromide. There was little reaction below 200°C. At this temperature however the reaction was complete in 12 h. The product was crystalline and gave: Ta, 39.4; Br, 55.9.

The product could, however, not be resublimed without decomposition. As previously stated, there is some evidence of a slow disproportionation into pentabromide and pentoxide even at 100°C and the fact that almost pure oxytribromide could be prepared by oxygenation at 200°C may be due to the inhibition of disproportionation by the excess of pentabromide present and the carrying forward of the product to a zone which is at slightly lower temperature.

The disproportionation increases rapidly as the temperature is raised, and heating at 450°C for 6 h resulted in the elimination of almost all the bromine.

References p. 216

In addition to the above methods of preparation, experiments were also carried out on the action of a carbon dioxide–bromine mixture on tantalum metal. These arose from an observation that when preparing tantalum pentabromide by the bromination of the metal using carbon dioxide as a carrier gas, black specks, later identified as carbon, appeared on the metal and a considerable amount of the product was relatively involatile. A mixture of carbon dioxide and bromine was passed over tantalum metal at 550°C and the resulting sublimate roughly fractionated at 180°C into a further sublimate, which gave: Ta, 31.5; Br, 67.9, and was therefore tantalum pentabromide [requires: Ta, 31.2; Br, 68.8], and a residue which gave: Ta, 45.2; Br, 49.2, and was chiefly oxytribromide. This was confirmed by X-ray diffraction, the sublimate giving only the lines of $TaBr_5$ and the residue those of $TaOBr_3$ and Ta_2O_5. The tantalum oxytribromide formed about 20% of the total product.

A similar effect was observed with aluminium, which shares with tantalum the property of forming a very resistant surface-layer of oxide. Whereas pure carbon dioxide did not have any observable effect on bright aluminium at 550°C, admission of bromine vapour into the carbon dioxide stream at this temperature, produced immediate darkening of the aluminium due to the separation of carbon, later identified as such by conversion into carbon dioxide by a stream of oxygen.

These results are significant as showing that at temperatures at which a metal may be resistant to attack by carbon dioxide alone, a reduction of the carbon dioxide may occur if a halogen is also present.

X-RAY ANALYSIS

Powder-diffraction photographs were taken of the three crystalline compounds, niobium oxytrichloride, niobium oxytribromide and tantalum oxytribromide, in a 19 cm diam. camera using Cu Kα radiation with a nickel filter (Fig. 3). Tantalum

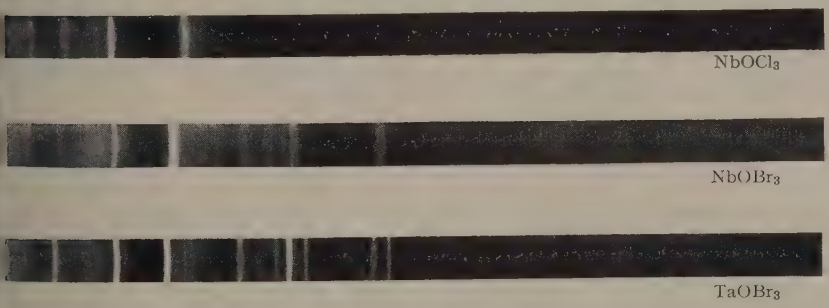

Fig. 3.

oxytribromide gave much the best photographs and, in addition to a number of very weak lines, the lines given in Table II were measured, intensities being estimated visually.

References p. 216

The diffraction patterns of the two oxytribromides are similar in many respects, the spacings of several of the strongest lines being almost identical. These two compounds are probably therefore isomorphous.

TABLE II

d/n		d/n	
8.21	vw	2.72	vw
6.93	vw	2.64	vw
5.21	s	2.27	m
3.63	vs	2.06	vw
3.55	w	1.99	s
2.9	vvs	1.91	m
2.80	vw	1.64	m
		1.59	s

s = strong, m = medium,
w = weak, v = very.

ACKNOWLEDGEMENT

We are indebted to Messrs. Imperial Chemical Industries Limited for the loan of the X-ray camera.

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THE URANIUM MONOCARBIDE–URANIUM MONONITRIDE SYSTEM

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SUMMARY

The system uranium monocarbide–uranium mononitride has been investigated by metallographic and X-ray diffraction techniques. Alloys were prepared by arc-fusion and by solid-state diffusion.

From the lowest temperature investigated, 1200°C, upwards, the carbide and nitride form a continuous series of solid solutions. At 1200°C the alloys prepared by solid-state diffusion obey Vegard's law but those prepared by fusion deviate from this law in a systematic fashion.

The results of X-ray diffraction studies of the diffusion process suggest that homogenisation occurs by solution of the carbide in the nitride, but not by the reverse process.

Uranium mononitride decomposes when melted in the argon-arc. An atmosphere containing 66% nitrogen does not suppress decomposition entirely.

Uranium monocarbide quenched from the melting point has a cell-size $\sim$ 0.1% less than that of the same material annealed at 1200°C.

INTRODUCTION

Uranium monocarbide and uranium mononitride both crystallize with the sodium chloride structure and their lattice parameters differ by approximately 1.4%. They would therefore be expected to show complete solid miscibility and the investigation to be described was undertaken to confirm this prediction. This system is also relevant to an understanding of the non-metallic inclusions found in uranium metal for reactors.

THE STRUCTURE OF ALLOYS PREPARED BY MELTING

Uranium mononitride was prepared by decomposition of the sesquinitride prepared from its elements.

Uranium powder prepared by calcium reduction of the oxide and freshly leached in 20% aqueous nitric acid solution, was loaded into alumina boats and weighed. Boats and contents were then heated to 800°C in one hour in a stream of cylinder nitrogen dried by anhydrone and phosphorus pentoxide, held at this temperature for 2 hours and then cooled. The weight gain corresponded to a nitrogen content slightly in excess of that present in U_2N_3.

The light grey sesquinitride powder in the alumina boats was transferred to a vacuum muffle furnace and heated at 1050°C for 2 hours. Rapid evolution of gas took place during heating to this temperature, but by the end of the soaking period the pressure had fallen to $\sim 10^{-5}$ mm Hg. The weight loss corresponded to a reaction

Reference p. 226

product of composition UN. X-ray diffraction analysis of the powder gave a sodium chloride structure of cell-size $a = 4.8897 \pm 0.0004$ Å. Its density determined by a vacuum pycnometric method was 14.0 g/cm³, the theoretical X-ray density being 14.3 g/cm³.

Uranium monocarbide was prepared by solid-state reaction of uranium and graphite. Powdered graphite prepared by machining pile quality blocks, and leached uranium powder were mixed together to give a carbon content slightly in excess of stoichiometry, and hot-compacted at 800°C and 15 tons/sq.in. pressure. The resulting compact of density 12.8 g/cm³ was then heated in high vacuum at 1050°C for 2 hours to give monocarbide of density 11.8 g/cm³. This material was crushed to powder under trichloroethylene in a percussion mortar. X-ray diffraction analysis of this powder gave a sodium chloride structure of cell size 4.9605 ± 0.0004 Å.

Alloy specimens were prepared by mixing the carbide and nitride powders, cold-compacting at 50 tons/sq.in., and then melting in an argon-arc, tungsten electrode furnace on a water-cooled copper-hearth. Two remelts were carried out to minimize segregation. Specimens of nominal uranium carbide contents 100%, 80%, 60%, 40%, 20% and 0% were prepared in this manner.

At all compositions smooth, shiny, dark-grey buttons were obtained. The densities of the melts were determined by water-displacement and the results are given in Table I. They show that the carbide is sensibly unaffected by melting, but that considerable dissociation of the mononitride must have occurred giving free uranium and nitrogen.

TABLE I

ANALYSES, DENSITIES AND LATTICE PARAMETERS OF ARC-MELTED ALLOYS

Spec. No.	*Nominal UN content w/o*	*Nitrogen analysis w/o*	*UN content by analysis w/o*	*Melt density g/cm³ (by displacement)*	*Density g/cm³ (from analyses)*	*Lattice constant Å*	*Lattice constant after 2 h vacuum annealing at 1250°C, Å*
A. Arc-melted in argon atmospheres							
3	0	—	—	13.44	—	4.9544 ± 0.0003	4.9544 ± 0.0002
4	20	0.28	5.03	14.44	14.94	4.9522 ± 0.0005	4.9522 ± 0.0003
5	40	0.84	20.14	14.67	15.04	4.9474 ± 0.0005	4.9476 ± 0.0003
6	60	1.00	31.03	15.57	15.36	4.9390 ± 0.0005	4.9385 ± 0.0003
7	80	1.1	49.75	16.30	16.30	4.9150 ± 0.0005	4.9150 ± 0.0003
8	100	1.3	23.40 w/o UN in U	16.49	17.45	4.8897 ± 0.0004	4.8897 ± 0.0003
B. Arc-melted in nitrogen–argon atmosphere							
15	0	—	—	13.22	—	4.9544 ± 0.0004	—
16	20	1.1	19.84	13.81	14.49	4.9474 ± 0.0003	—
17	40	1.6	32.43	13.94	15.05	4.9410 ± 0.0003	—
18	60	1.63	42.31	14.50	15.23	4.9280 ± 0.0004	—
19	80	2.2	66.44	14.08	15.48	4.9083 ± 0.0004	—
21	95	2.3	89.22	14.23	15.79	4.8938 ± 0.0004	—
14	100	3.6	56.61 w/o UN in U	14.37	15.91	4.8890 ± 0.9004	—

Reference p. 226

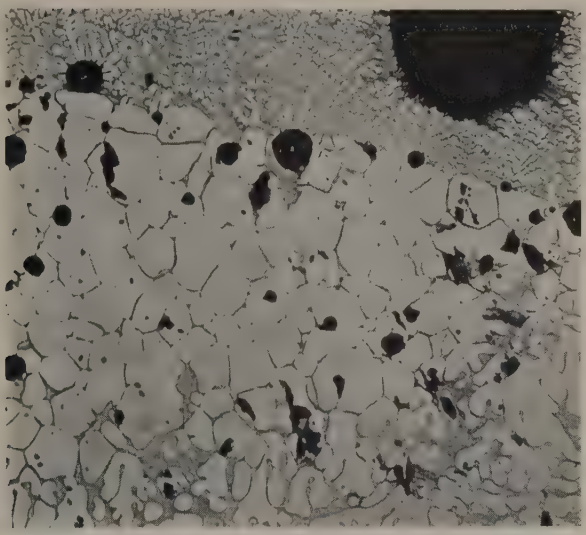

Fig. 1. Uranium mononitride, argon-arc melted showing core and shell with uranium matrix (× 140).

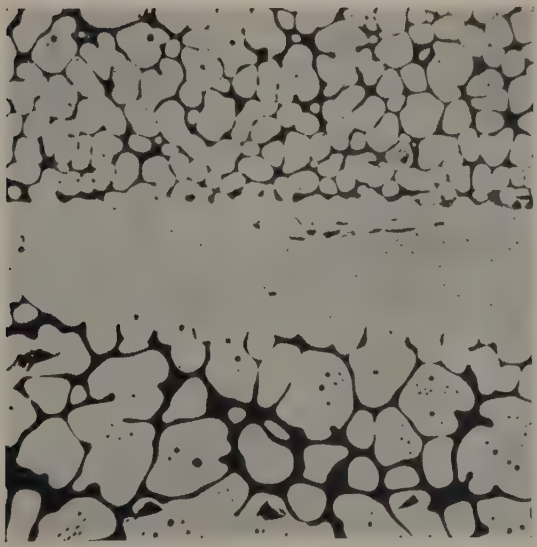

Fig. 2. 80 Wt.-% uranium monocarbide alloy showing end of core and shell (× 350).

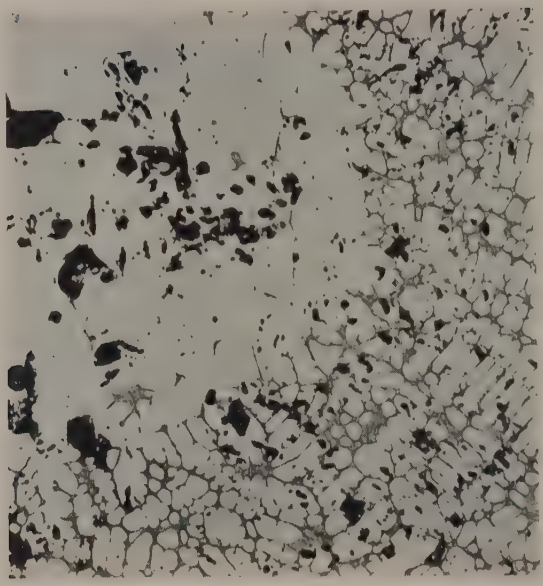

Fig. 3. Uranium mononitride melted in a nitrogen–argon atmosphere (compare with Fig. 1) (× 140).

Fig. 4. 80 Wt.-% uranium monocarbide alloy arc-melted in a nitrogen–argon atmosphere (compare with Fig. 2) (× 350).

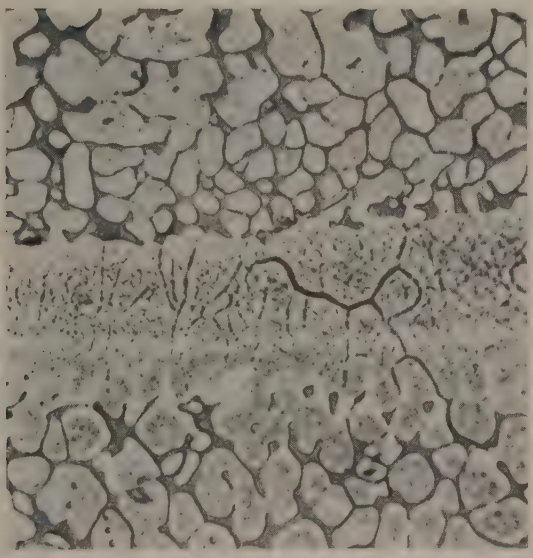

Fig. 5. 80 Wt.-% uranium monocarbide alloy showing end of core and shell. Etched in nitric–acetic acid. Granular effect due to deposition of carbon (× 350).

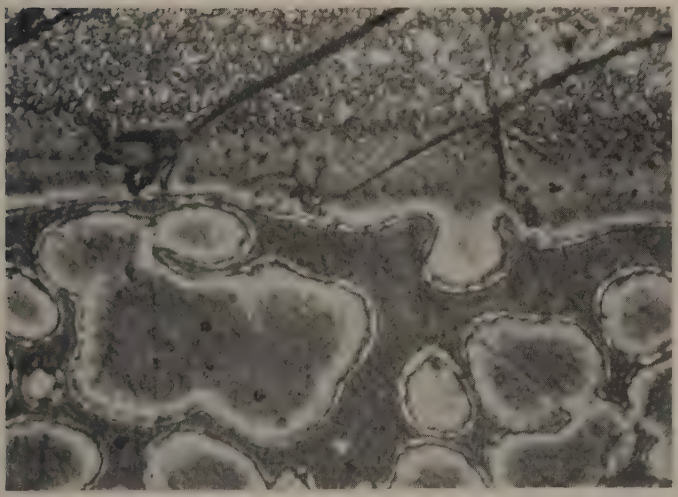

Fig. 6. 60 Wt.-% uranium carbide alloy, etched to show "coring" (× 1600).

An attempt was made to suppress this dissociation by using a partial pressure of nitrogen in the arc-furnace atmosphere. To be able to strike and maintain an arc a minimum content of one part argon in two parts of nitrogen was found necessary. A second series of alloy specimens was prepared in this atmosphere. Their respective densities given in Table I indicated that dissociation was inhibited if not eliminated.

All specimens were sectioned and polished for metallographic examination. Coarse grinding was carried out on a diamond impregnated wheel, fine grinding on carborundum paper lubricated with paraffin and final polishing on felt laps using graded diamond paste abrasives. Great care had to be taken to avoid chipping of the surface, which under a microscope showed up as angular voids.

For all specimens a two-phase structure was seen on microscopical examination. Traces of the dicarbide were found in the specimen of nominal composition 100% UC, but it was not observed in any of the pseudo-binary UC–UN alloys. These latter and the nominal 100% UN specimen all consisted of a core containing hard particles with small amounts of a softer intergranular material and a softer shell made up of dendrites of the harder constituent in a matrix of the softer material (Figs. 1 and 2). The effect of the nitrogen addition to the melting atmosphere in diminishing the amount of soft phase is illustrated in Figs. 3 and 4. The etching characteristics of the specimens in air and a mixture of 1:1:1 conc. nitric acid–acetic acid–water indicated that the softer intergranular phase was uranium. The latter etchant revealed coring in the hard constituent, the centre of the particles being apparently carbon rich (Figs. 5 and 6). In Fig. 6, a light rim appears around the cored particle but this was not consistently produced and was therefore deemed to be an etching artefact.

X-ray analysis of the various ternary alloys and UN confirmed the presence of free uranium. Apart from this free uranium pattern a single sodium chloride type pattern was obtained in all cases. For the as-melted samples line broadening and poor resolution of doublets became progressively worse as the nitrogen content of the melts increased. This could have been due to strain or to the 'coring' observed metallographically. The samples were therefore annealed for 2 hours at 1250°C. Diffraction patterns of good resolutions were obtained after this treatment, with no measurable effect on the lattice parameters. These parameters, given in Table I show a gradual decrease in moving from the pure monocarbide to the pure mononitride composition.

Approximately half of each sample was submitted for chemical analysis for nitrogen estimations. The nominal and true compositions are given in Table I together with the density calculated from the true composition.

In Fig. 7 the cell-size is plotted against composition for alloys melted in argon and in the argon–nitrogen mixture. The results deviate from the straight line relationship expected from Vegard's law but to no greater extent than is commonly observed in mixed monocarbide systems[1].

THE STRUCTURE OF ALLOYS PREPARED BY SOLID-STATE DIFFUSION

Alloy preparation by solid-state diffusion was investigated because of the dissociation of uranium mononitride when melted in the argon-arc and because of segregation difficulties.

Reference p. 226

Powder mixes containing 80, 50 and 10 w/o UC were cold-pressed at 40 tons/sq.in. giving rather fragile compacts, which were annealed in an alumina boat in vacuo (5×10^{-5} mm Hg) at 1200°C for varying times.

The homogenization process was followed by X-ray powder diffraction analysis. For the 80 and 10 w/o UC alloys after 48 hours there was no trace of the original carbide and nitride patterns, but the single cubic pattern present was poorly resolved. Increase of annealing time up to 448 hours for these alloys improved the resolution of the solid solution's pattern, but longer times caused no further change in definition of the diffraction pattern.

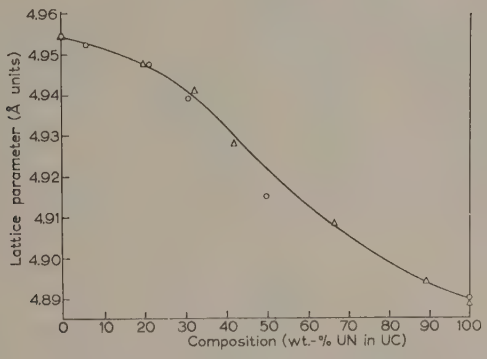

Fig. 7. Lattice constants of the UC–UN system (fused alloys).
△ Arc-melted in argon atmosphere.
○ Arc-melted in argon–nitrogen atmosphere.

After 48 hours annealing, the 50 w/o alloy gave two cubic diffraction patterns one of which corresponded in spacing to the original carbide pattern and the other to a structure intermediate in cell-size between carbide and nitride. Further annealing of this alloy for 144, 216 and 312 hours considerably diminished the intensity of the carbide pattern which however still showed no change in cell-size. The second, UC–UN solid solution, pattern steadily expanded in cell-size and the line definition improved with increasing annealing time. After 468 hours the carbide pattern vanished. The d-spacings of three high-angle lines are given in Table II for the 50 w/o alloy

TABLE II

DETAILS OF SHIFTS IN d-SPACINGS AFTER SUCCESSIVE ANNEALINGS OF 50/50 W/O POWDER MIXTURE

UC	UC pattern				UN	UC–UN pattern			
	48 h	144 h	216 h	312 h		48 h	144 h	216 h	312 h
0.784	0.783	0.783	0.783	0.783	0.773	0.776	0.777	0.778	0.779
0.827	0.826	0.824	0.824	0.824	0.815	0.817	0.816	0.819	0.820
0.836	0.836	0.836	0.836	0.836	0.827	0.829	0.830	0.831	0.832

Reference p. 226

after various annealing times. The absence of change in spacing of the carbide pattern is appararent, whilst the spacing of the other pattern moves slowly from that of the nitride to a position intermediate between nitride and carbide.

Further investigation of the structure of the 50 w/o alloy at the various stages of homogenization already detailed, using a Geiger spectrometer to determine line profile and spacing, confirmed the visual observations. During annealing the profiles of the high angle lines examined remained fixed in position for the carbide but the peak height diminished with annealing time. The profiles corresponding originally to nitride lines gradually moved to a position midway between the carbide and original nitride lines, and increased in area (both height and width).

No free uranium was detected in any specimen. The homogenization process in the 10 w/o and 80 w/o UC specimens had been completed by the time that the first diffraction patterns were obtained (48 hours) and so no evidence of the anomalous shift in lines was obtained in these specimens. Specimens containing 80 w/o and 10 w/o UC were therefore prepared as before and annealed in vacuum for times of $^1/_2$, 1, 2 and 4 hours. The diffraction patterns were determined after each anneal.

The 10 w/o UC alloy showed the marked behaviour already described for the 50 w/o alloy, and it could also be detected, although less obvious, in the 80 w/o alloy.

The lattice parameters for the various alloys after successive annealing are given in Table III and plotted in Fig. 8, which shows that Vegard's law is obeyed with a good degree of accuracy.

TABLE III

LATTICE PARAMETERS AFTER SUCCESSIVE ANNEALINGS OF POWDER MIXTURES

Time in hours	*All values within ± 0.0004 Å units*				
	UC	*80/20 w/o*	*50/50 w/o*	*10/90 w/o*	*UN*
As prepared	4.9604	—	—	—	4.8898
72	4.9606	—	—	—	4.8906
400	—	4.9471	4.9257	4.8967	—
448	—	4.9484	4.9270	4.8975	—
510	4.9606	4.9486	4.9271	4.8974	4.8906

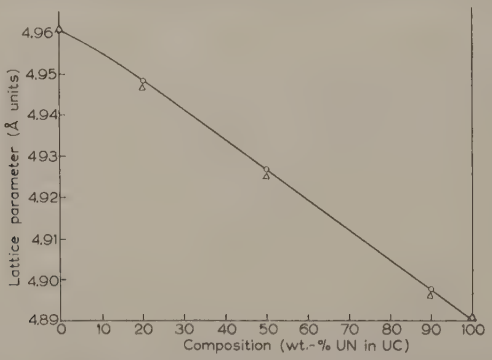

Fig. 8. Lattice constants of the UC–UN system (diffusion alloys).
△ Solid-state reaction after 400 h at 1200°C.
○ Solid-state reaction after 448 h at 1200°C.

Reference p. 226

DISCUSSION

Uranium carbide and uranium nitride exhibit complete solid-state miscibility at 1200°C and above.

Vegard's law is obeyed by the alloys prepared by solid-state diffusion, but those prepared by fusion deviate from a linear relationship between cell-size and composition. Although due to segregation, lack of correspondence between the sample analysed and that taken for diffraction studies could lead to such deviations, the symmetry and opposing nature of the deviations about the 50:50 alloy discount such an explanation.

A further difference between the parameters of alloys of the same composition prepared by fusion and by solid-state diffusion must result from the variation in lattice parameter of the monocarbide prepared by these two techniques.

Monocarbide prepared by reaction of uranium and graphite at 1050°C had a cell-size of 4.9606 ± 0.0004 Å. The same powder after arc-fusion had a cell-size of 4.9544 ± 0.0003 Å. Annealing of this fused powder at 1250°C for two hours produced no change in parameter, but after annealing for 72 hours at 1200°C the cell-size expanded to 4.9606 ± 0.0003 Å; increase of annealing time to 510 hours produced no further change. Similar annealing treatments of fused uranium nitride produced no change in lattice parameter but only an improvement in resolution of the pattern.

Investigation of the range of homogeneity of the monocarbide at higher temperatures is desirable.

Interdiffusion of the monocarbide and mononitride, on the evidence of diffraction data, takes place by solution of the carbide in the nitride but not by the reverse process. Gross segregation of the monocarbide would be needed to give rise to the observed effects, and this appears improbable. Dissociation of the nitride or chemical interaction of carbide and nitride would not produce the sequence of line-shifts observed.

These results imply not only that the rates of interdiffusion of carbide and nitride differ appreciably but also that the carbide diffuses as the complex UC. Uranium mononitride may deviate from stoichiometry on the nitrogen-rich side of its composition and thus be able to dissolve carbon, but there is no evidence that the carbide exhibits any variation in composition in either direction at 1200°C. There are therefore no mechanisms by which interdiffusion due to movement of carbon or nitrogen atoms, or vacancies alone, could explain the experimental results.

Similar results have not been reported for other carbide–nitride systems[1], perhaps because the investigators were directly interested in the equilibrium structures and not in the process by which this equilibrium was achieved.

CONCLUSIONS

Uranium monocarbide and uranium mononitride form a continuous series of solid solutions at temperatures upwards of 1200°C. Vegard's law relating lattice parameter to composition is accurately obeyed for alloys prepared by diffusion at 1200°C, but those prepared by fusion deviate from this law in a regular manner. The results of X-ray diffraction studies suggest that interdiffusion of the carbide and nitride occurs by solution of the carbide in the nitride but not by the reverse process.

Reference p. 226

Uranium mononitride decomposes when melted in the argon-arc, and at such temperatures possesses a vapour pressure of nitrogen greater than $^2/_3$ atmosphere of nitrogen.

The lattice parameter of uranium monocarbide quenched from the molten state is 0.1% less than that of the same material annealed at 1200°C.

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KINETICS OF THE OXIDATION OF URANIUM BY CARBON DIOXIDE

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SUMMARY

The rates of oxidation of uranium by carbon dioxide have been determined over the range 500–1000°C. The rate increases with temperature from 500 to 780°C with a sudden marked increase when the metal is near or at the β–γ transition (772°C). At higher temperatures up to 1000°C the rate decreases with increasing temperature.

The reaction obeys a linear rate law for the range 500–800°C, although self-heating sometimes results in a non-linear weight increase–time graph. In the range 500–725°C the activation energy is 26 $\pm$ 10 kcal/mole which is consistent with oxygen ion diffusion being the rate controlling mechanism.

INTRODUCTION

The power reactors at present being built in the United Kingdom are fuelled with uranium metal and cooled by carbon dioxide. Although the fuel is contained in a magnesium alloy can, the compatibility of the fuel with the coolant can be of importance in the event of a can being defective.

Data have been published on the oxidation of uranium by air, oxygen, and steam but little are available on the reaction with carbon dioxide. This paper is concerned with the provision of data for this reaction in the temperature range 500–1000°C.

Thermodynamic calculations show that large free energy and heat changes favour the reaction of uranium with carbon dioxide to form uranium dioxide and either carbon monoxide or carbon. The deposition of carbon would probably take place via the reduction of carbon monoxide and should therefore depend upon the experimental conditions; if the supply of gas were restricted carbon formation would be expected, whilst with a fast flowing gas the major proportion of the carbon monoxide would be swept away before reacting. Any carbon formed might react with the metal to give the carbides UC or UC_2. All the results in this paper refer to experiments conducted with a fast flowing gas at one atmosphere pressure.

EXPERIMENTAL METHOD AND RESULTS

The reaction was followed by continuous weighing of the uranium specimens in a stream of gas (200–500 c.c./min) in a thermal balance as described by KUBASCHEWSKI AND HOPKINS[1]. The gas was preheated to the experimental temperature and the specimen was contained in an alumina crucible to retain the nonadherent product. A thermocouple in a silica pocket adjacent to the specimen measured the gas temperature which was less than the specimen temperature by an amount dependent upon the degree of self-heating caused by the exothermic nature of the reaction.

References p. 231

The specimens were discs of calcium and magnesium reduced uranium which had been pickled in dilute nitric acid and washed in water and acetone before use. They weighed 11–140 g and had surface areas of 4–22 cm^2. The source of gas was volatilised "cardice" which contained up to 400 v.p.m. oxygen and 900 v.p.m. water vapour as its major impurities. The effect of water vapour was determined by using gas dried with anhydrous magnesium perchlorate (< 20 v.p.m. H_2O), undried gas and gas saturated with water vapour at room temperature (3.1 vol.-% H_2O).

With gas temperatures of 500–900°C the product was nonadherent and powdery and shown by X-ray analysis to be uranium dioxide with a larger particle size the higher the temperature; uranium carbides and higher oxides (*e.g.* $UO_{2.25}$ and U_3O_8) were not detected. At 1000°C the product was in the form of a scale with a bulk density of 10.1 g/c.c.

Water vapour had only a slight effect. 3.1 vol.-% H_2O increased the attack at 500°C by a factor of 8–32 but the effect at higher temperatures and of the small amounts of water present in undried gas was less than the experimental error.

The rates of attack are summarized in Table I and Fig. 1 and typical weight increase–

TABLE I

REACTION RATES OF URANIUM WITH CARBON DIOXIDE CONTAINING < 20–900 v.p.m. WATER VAPOUR EXPRESSED AS A RATE OF WEIGHT GAIN IN $mg/cm^2/h$

Gas temperature °C	*Reaction rate mg wt. gain/cm^2/h*
500	0.25, 0.4, 0.5, 1.0, 1.0, 1.4
650	4.1, 13.5
680	5.0, 3.2–6.0
700	6.1, 23–57, 26–540, 73
709	122
725	48.5, 56–510, 115–580
750	586
755	423
790	480
800	280, 280, 550
860	470, 480
900	220, 240, 300
1000	160, 170

time graphs for 500°, 725° and 1000°C are shown in Figs. 2, 3 and 4 respectively.

At 500°C a linear rate was obtained characteristic of a non-protective oxide, whilst at 700–750°C a slow linear rate was suddenly replaced by a fast one. The time taken to reach the change point varied with the size of the specimen and the temperature and was believed to be linked with self-heating of the uranium. To investigate self-heating the temperature in the centre of a large specimen (2.5 cm long and 2 cm diameter) was measured, by placing a thermocouple in a 3 mm diameter hole in the specimen, whilst the gas was at 700–725°C. The result is shown in Fig. 5. Self-heating was not obtained until the gas reached 725°C; the temperature of the specimen then gradually rose until a sudden marked increase of 150°C was obtained when it reached 775–780°C. It was not possible to measure self-heating and weigh the specimen at the same time but the sudden increase in temperature of the specimen when it reached

References p. 231

775–780°C is believed to coincide with the increase in reaction rate by a factor of ten. From the rate of rise of the temperature of the specimen between 725 and 775°C it can be calculated that the temperature gradient across the specimen was less than 1°C for specimen temperatures below 775°C. The temperature at the surface of the metal when a sudden increase in rate was obtained was therefore 775–781°C and the final fast rates with lower gas temperatures were due to self-heating.

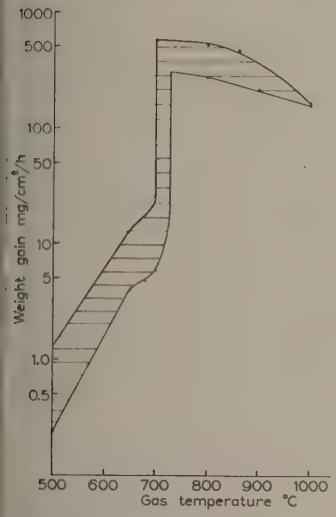

Fig. 1. Relation between reaction rate and temperature.

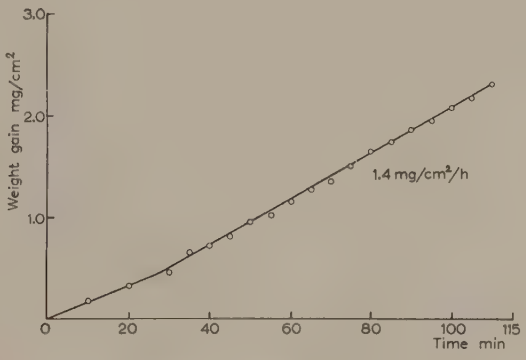

Fig. 2. Oxidation of uranium in CO_2 at 500°C.

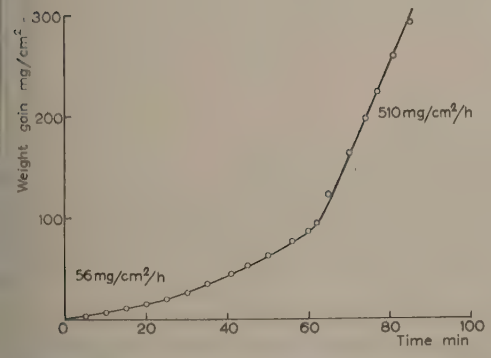

Fig. 3. Oxidation of uranium in CO_2 at 725°C.

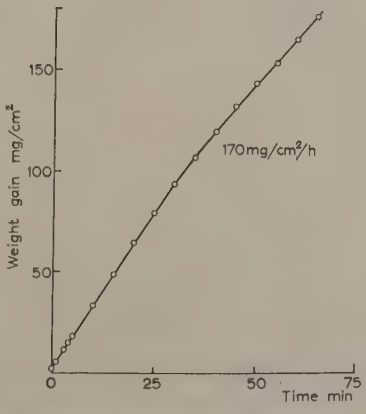

Fig. 4. Oxidation of uranium in CO_2 at 1000°C.

References p. 231

In the range 800-1000°C the rate decreased with increasing temperature and at 1000°C the weight increase–time graphs were slightly curved.

The reproducibility of the rates was not good; this was partly due to the different behaviour of different batches of metal, which was attributed to variations in impurity content and distribution. The extremely bad consistency at 700–725°C was the result of self-heating.

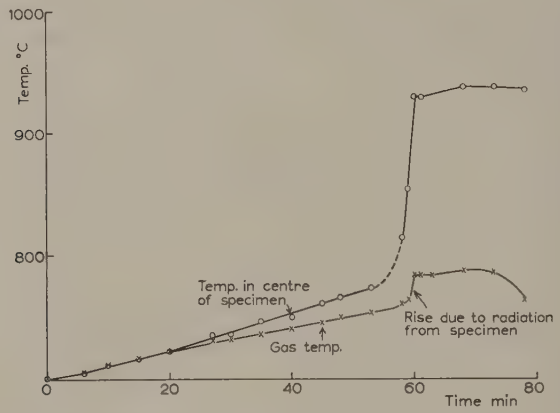

Fig. 5. Self-heating of uranium in carbon dioxide at 700–725°C.

DISCUSSION

The linear portions of the weight increase–time graphs indicate that a linear rate law is obeyed in the range 500–800°C. An Arrhenius plot of all the data for which self-heating was negligible, gives an activation energy of 26 ± 10 kcal/mole in the range 500–725°C. Oxygen ions are believed to be the diffusing species in uranium dioxide, and therefore three possible rate determining steps which satisfy a linear rate law are:

(i) transfer of oxygen atoms from the gas to a thin adherent film of uranium dioxide.

(ii) diffusion of oxygen ions through an oxide film followed by cracking once a limiting thickness is reached.

(iii) reaction at the oxide–metal interface.

The activation energy is in reasonable agreement with the value of 29.7 ± 2.3 kcal/mole[2] obtained for the self-diffusion of oxygen ions in uranium dioxide. Oxygen ion diffusion is therefore believed to be the rate controlling step in the range 500–725°C. The data are inconsistent with uranium ion diffusion as this process requires an activation energy > 90 kcal/mole[3].

The slight curvature in the weight increase–time graph at 1000°C could be due to the gas having to diffuse through the adherent, porous scale and hence to a change in the rate determining step. This is corroborated by the reduction in rate on increasing

References p. 231

the temperature from 800 to 1000°C. The protective scale could be produced by sintering of the powdery oxide or by a thickening of the stable uncracked film thickness, as the oxide should be more plastic at the higher temperatures and hence able to reduce stresses by deformation rather than cracking. The former mechanism is unlikely to be the only one operative as sintering of uranium dioxide is not appreciable until 1300°C, whilst the bulk density of the scale at 1000°C was 93% of the maximum value possible.

The sudden increase in rate at 700–750°C is similar to that obtained by HOPKINSON[4] for the uranium–steam reaction at 700°C. Unfortunately HOPKINSON only measured gas temperatures and did not establish the temperature of the metal at which the increase occurred. The similarity between the two reactions indicates that the effect is associated with the metal or oxide, not the gas. In the self-heating experiment the increase occurred when the metal reached 775–781°C which almost corresponds with the value of 772° given for the β–γ transition temperature for slowly heated uranium. The most plausible explanation for the increase in rate is that the adherence of the thin uncracked oxide is destroyed by the transition.

CONCLUSIONS

The reaction rate of uranium with carbon dioxide increases with temperature from 500 to 780°C with a sudden increase when the metal is near or at the β–γ transition. At higher temperatures up to 1000°C the rate decreases with increasing temperature due to the formation of a thick oxide barrier between the gas and metal.

Appreciable self-heating of the metal, with temperature rises of up to 190°C, may be obtained with gas temperatures of 700–1000°C.

The reaction obeys a linear rate law for the range 500–800°C, although self-heating sometimes results in a non-linear weight increase–time graph. In the range 500–725°C the activation energy is 26 $\pm$ 10 kcal/mole which is consistent with oxygen ion diffusion being the rate controlling mechanism.

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PROPERTIES OF TITANIUM–ALUMINIUM–NIOBIUM ALLOYS

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SUMMARY

The addition of niobium to a binary titanium–aluminium alloy results in increased strength at temperatures up to 500°C. If the alloy contains 10 at.-% niobium then the strength at low temperatures can be raised by heat treatment. Still higher strengths can be obtained by the use of poorer grades of sponge titanium without much sacrifice in ductility.

Recently some attention has been directed to the properties of binary alloys of titanium with niobium[1,2,3]. It was shown that additions of niobium have a moderate strengthening effect on titanium both at room and at elevated temperatures. The present work deals with the effects of niobium additions on the properties of a titanium–aluminium alloy. The effects of heat treatment and of impurities on the mechanical properties are also reported.

EXPERIMENTAL

In the three alloys studied the aluminium content was 12 at.-% and the niobium content was either 0, 5 or 10 at.-%. The alloys were prepared by arc melting together high purity aluminium, commercial purity niobium and sponge titanium (hardness 105 V.H.N.). For some experiments other grades of titanium sponge were used (hardness 170 and 225 V.H.N.). The 40 g ingots were swaged at 800°C to rod of 0.25 in. diameter from which test bars were machined with a reduced section 1 in. by 0.125 in. diameter.

RESULTS

(*a*) *Room temperature properties*

The binary titanium–aluminium alloy had a elongation to fracture of 20% and a U.T.S. of 100,000 p.s.i. and these properties were not affected by heat treatment.

Table I shows the effects of heat treatment on the mechanical properties of the alloy containing 12 at.-% Al and 5 at.-% Nb. The solution treatment temperatures were chosen to give a wide range in the amount of primary α phase. Relatively high ageing temperatures were selected so that the alloys might be stable at elevated temperatures although such ageing treatments might lead to some softening due to over-ageing. It can be seen that the effect of these heat treatments on the room

References p. 236

TABLE I

PROPERTIES OF Ti–12 at.-% Al–5 at.-% Nb AT 22°C

Heat treatment	*Primary α phase (%)*	*U.T.S. (p.s.i.)*	*Elong. (%)*
½ h 930°C WQ	63	158,000	11
½ h 930°C WQ age 24 h 550°C	63	160,000	10
½ h 930°C WQ age 24 h 575°C	63	159,000	11
½ h 930°C WQ age 24 h 600°C	63	158,000	10
½ h 960°C WQ	41	158,000	8
½ h 960°C WQ age 24 h 550°C	41	169,000	9
½ h 960°C WQ age 24 h 575°C	41	164,000	8
½ h 960°C WQ age 24 h 600°C	41	163,000	8
½ h 990°C WQ	7	152,000	9
½ h 990°C WQ age 24 h 550°C	7	164,000	9
½ h 990°C WQ age 24 h 575°C	7	160,000	8
½ h 990°C WQ age 24 h 600°C	7	157,000	9

temperature properties is quite small. Although the strength increases with decreasing ageing temperature it is not expected that any substantial increase in the strength of this alloy is likely as a result of ageing at lower temperatures.

The Ti–12 at.-% Al–10 at-% Nb alloy shows reasonable response to heat treatment (Table II). For solution treatment temperatures in the range 820–870° C the

TABLE II

PROPERTIES OF Ti–12 at.-% Al–10 at.-% Nb AT 22°C

Heat treatment	*Primary α phase (%)*	*U.T.S. (p.s.i.)*	*Elong. (%)*
½ h 820°C WQ	56	153,000	13
½ h 820°C WQ age 24 h 550°C	56	185,000	10
½ h 820°C WQ age 24 h 575°C	56	181,000	8
½ h 820°C WQ age 24 h 600°C	56	174,000	8
½ h 870°C WQ	34	147,000	12
½ h 870°C WQ age 24 h 550°C	34	179,000	8
½ h 870°C WQ age 24 h 575°C	34	181,000	7
½ h 870°C WQ age 24 h 600°C	34	180,000	5
½ h 910°C WQ	10	150,000	12
½ h 910°C WQ age 24 h 550°C	10	217,000	3
½ h 910°C WQ age 24 h 575°C	10	206,000	3
½ h 910°C WQ age 24 h 600°C	10	197,000	3

properties are remarkably uniform and it is only when the solution treatment temperature is raised to 910°C that the strength in the aged condition increases and the ductility decreases sharply. An example of the micro-structure of these alloys is given in Fig. 1. After quenching the structure consists of primary α and a mixture of retained β and martensitic α.

Figs. 2(a), (b) and (c) show the effects of using different grades of sponge titanium

References p. 236

Fig. 1. Ti–12 at.-% Al–10 at.-% Nb alloy after solution treatment at 910°C and ageing at 575°C (× 1000). (Light etching phase — primary alpha.)

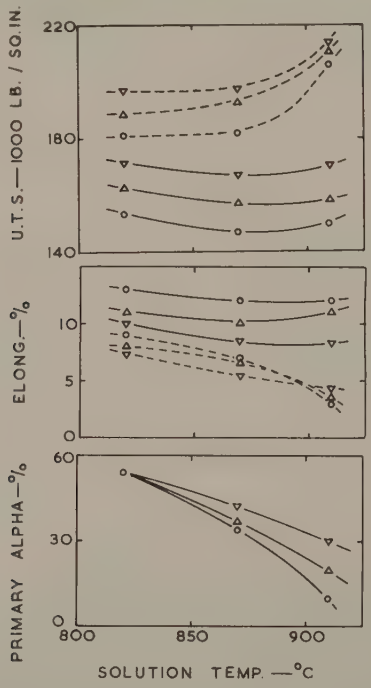

Fig. 2. Effect of impurities on the properties of Ti–12 at.-% Al–10 at.-% Nb after heat treatment.

○ Basis Ti 105 V.H.N. Broken line after "ageing".
△ Basis Ti 170 V.H.N. Full line "as quench".
▽ Basis Ti 225 V.H.N.

(hardness 105, 170 and 225 V.H.N.) on the properties of the alloy containing 12 at.-% Al and 10 at.-% Nb, after various heat treatments. In the "as quenched" condition, increasing impurity content (mainly oxygen) of the titanium increases the strength and decreases the ductility of the alloy almost independently of the solution treatment temperature. However, in the aged condition, ageing response decreases with increasing impurity content after solution treatment at 910°C. This effect is related to the effect of impurity content on the amount of primary α present after solution treatment. It is only when the solution treatment temperature is greater than 870° C that the presence of the additional impurities in the titanium greatly affects the amount of primary α phase present after solution treatment and thus the response to heat treatment.

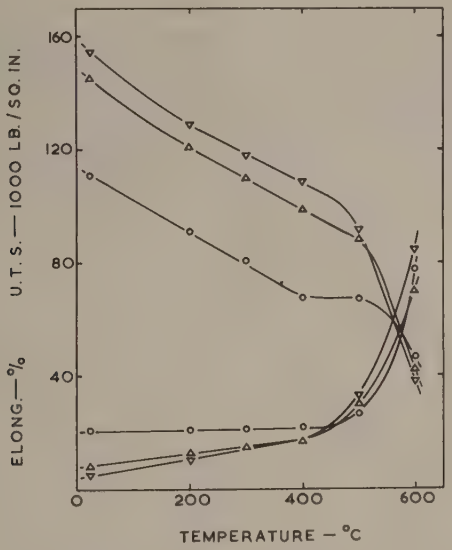

Fig. 3. Properties of Ti–Al–Nb alloys at elevated temperatures.

○ Ti–12 at.-% Al– 0 at.-% Nb
△ Ti–12 at.-% Al– 5 at.-% Nb
▽ Ti–12 at.-% Al–10 at.-% Nb

(b) Elevated temperature properties

Fig. 3 shows the properties of the three alloys, based on titanium of hardness 225 V.H.N., at elevated temperatures. Before testing the alloys were annealed at 650°C for 16 hours. The properties of the binary titanium–aluminium alloy have been discussed previously[4]. The addition of 5 at.-% niobium results in a considerable increase in strength at temperatures up to 500°C. Increasing the niobium content to 10 at.-% increases the strength only slightly and it is not expected that further increases in niobium content will result in any marked increase in strength. At tem-

References p. 236

peratures above 500°C the strengthening effect of the niobium additions disappears. Although the strength of these alloys at low temperatures can be increased by suitable heat treatment, it is not likely that such heat treatments, involving ageing at temperatures in the range 5–600°C, will improve the properties of these alloys at temperatures above 500°C.

ACKNOWLEDGEMENT

The investigation formed part of the programme of research of the Physical Metallurgy Section of the Commonwealth Scientific and Industrial Research Organisation, Australia. The work was carried out at the Baillieu Laboratory, University of Melbourne under the general direction of Professor H. W. WORNER to whom the author expresses his thanks.

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A SPECTROPHOTOMETRIC INVESTIGATION OF THE NIOBIUM PROTOCATECHUIC ACID COMPLEX

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SUMMARY

Freshly precipitated niobium pentoxide will react with alkaline protocatechuate solution to produce a yellow, water-soluble complex. It was established by spectrophotometric means that a 1:1 niobium to PCA ratio exists in 0.01 molar protocatechuate solutions. The formation constant of this species at pH 10 was determined to be 1.05×10^3.

This complex compound was found to be more stable than the analogous niobium complexes with pyrogallol and catechol.

A solid niobium–protocatechuato complex was isolated and its formula postulated to be $(NH_4)_4H_2[NbO(PCA)_3]\cdot 4H_2O$.

INTRODUCTION

The color reactions of niobium species with polyphenols[1,2] in water solution have been known for some time, and occasionally have provided convenient analytical methods for determination of this metal.

In a few instances, solid compounds have been isolated and their compositions determined[1,3]. Only recently, however, in the cases of the niobium–pyrogallol[4], niobium–sulfosalicylate[5], and the niobium–catechol[3] complexes, has information concerning the complex ion in solution been determined and formation constants calculated.

To further extend existing knowledge concerning the chemical constitution of aqueous niobium–polyphenol complexes, the reaction between niobium pentoxide and protocatechuic acid** (3,4-dihydroxybenzoic acid) was studied by spectrophotometric means. The selection of the protocatechuate ion as a complexing ligand was prompted by an interest in the influence of the carboxyl group on the coordinating ability of the adjacent OH groups, as compared to that of catechol and pyrogallol. Apparently, the employment of PCA as a coordinating ligand for metal ions has been reported only with UO_2(II)[6], Cr(III)[7] and Fe(II) and (III)[8–10].

By using a modification of the methods developed by NEWMAN AND HUME[11], it was possible to show that a definite complex was present in the range of concentrations studied and to calculate a formation constant.

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** The symbol PCA has been employed throughout this paper for the protocatechuato ligand, $C_7H_3O_4^{---}$.

References p. 243

EXPERIMENTAL

Measurements

Absorption measurements in the ultraviolet region were made at room temperature with a Beckman DK-2 Automatic Recording Spectrophotometer. A pair of matched 1 cm silica cells fitted with 0.9 cm silica plugs was used for all measurements. A reference blank was used in all cases, and its preparation and composition were identical with the complex solution except that the niobium was missing.

pH measurements were made with a Beckman Model GS pH meter, equipped with a calomel and glass electrode. The instrument was standardized against a special buffer solution supplied by the manufacturer.

Materials

Protocatechuic acid (Aldrich Chemical Co., Milwaukee 12, Wisc.) was purified by recrystallization twice from hot water, using 3 ml water per g of acid and 1 g activated charcoal for every 10 g of acid. The purified product was a light cream color, m.p. = 204°C. All other chemicals used were reagent grade.

Solutions for ultraviolet absorption studies were prepared as follows: 0.05 g of Nb_2O_5 (Fairmount Chemical Co., Newark, N. J.) was fused in a Vycor crucible with 1–2 g $KHSO_4$. After cooling slightly, the warm crucible was added to 200 ml hot 2% HCl solution on a hot plate. The crucible and its contents were digested for 30 minutes, then the precipitated oxide was filtered on a Büchner funnel and washed with 200 ml hot water, followed by an acetone rinse. This hydrous oxide was then placed in a 250 ml round bottom flask equipped with a reflux condenser, and gently heated with 200 ml 0.01 *M* sodium protocatechuate until dissolved.

The sodium protocatechuate solution was prepared by dissolving 50 g Na_2SO_3 in water in a 500 ml volumetric flask. 0.7706 g protocatechuic acid was added along with 50 ml 0.1 *N* NaOH. The volume was then made up to 500 ml with distilled water.

For dilutions, a solution containing 100 g Na_2SO_3 per liter was used.

Solutions were prepared for spectrophotometric scan as follows: using a buret, seven 4 ml portions of the niobium-containing complex solution were measured into small ground glass stoppered bottles. Keeping the total volume of each solution 50 ml, increasing amounts of 0.01 *M* sodium protocatechuate and decreasing amounts of Na_2SO_3 solution were added to vary the PCA concentration of the respective solutions from 0.8×10^{-3} to 5.6×10^{-3} *M*, each solution containing the same molar concentration of niobium (1.023×10^{-4} *M*). Reference solutions were prepared in exactly the same manner, differing from the first only in that they contained no niobium. Data taken from the curves obtained from these solutions are shown in Table I.

As explained previously[3] the large, fixed concentration of Na_2SO_3 served not only as an antioxidant, but also to maintain constant ionic strength and pH (approximately 10). As would be expected, the stability of the sodium protocatechuate solutions was somewhat greater than that for catechol. However, for greatest accuracy, a standardized procedure was again employed, so that approximately the same length of time elapsed between preparation of solution and absorption measurements.

References p. 243

Isolation of the complex

Several unsuccessful attempts were made to isolate the ammonium salt of the niobium–PCA complex, utilizing the procedure used for preparation of the analogous catechol compound. This salt was finally isolated by the following procedure: 3.7 g of protocatechuic acid was dissolved in 40 ml conc. NH_4OH solution in a three-neck flask. 1 g of freshly precipitated Nb_2O_5 was added and the mixture heated gently, during which time nitrogen was bubbled through the reaction mixture to retard oxidation. When all Nb_2O_5 had dissolved and the solution was cooled, addition of an equal volume of acetone resulted in formation of a viscous red oil. The supernatant liquid was decanted and the oil washed repeatedly with acetone. The thick mass was then placed in an Abderhalden dryer and dried several hours under reduced pressure at 64°C. The red dried material was a very hard, brittle solid, which apparently undergoes no decomposition on standing.

The N : Nb : C ratio was found by analysis to be 4.1 : 1 : 20.0, suggesting the empirical formula $(NH_4)_4H_2[NbO(PCA)_3]\cdot 4H_2O$.

Anal. Calculated for $(NH_4)_4H_2[NbO(PCA)_3]\cdot 4H_2O$:
Nb, 13.11%; C, 35.60%; H, 4.98%; N, 7.90%.
Found:
Nb, 13.35%; C, 34.59%; H, 5.04%; N, 8.29%.

Analysis

Analysis of niobium-containing complex solutions was accomplished spectrophotometrically as previously described[3], utilizing the absorption of the Nb–HCl complex at 281 mμ[12].

The niobium content of the isolated solid complex was determined by igniting the sample in a previously weighed crucible. The residue was weighed as Nb_2O_5.

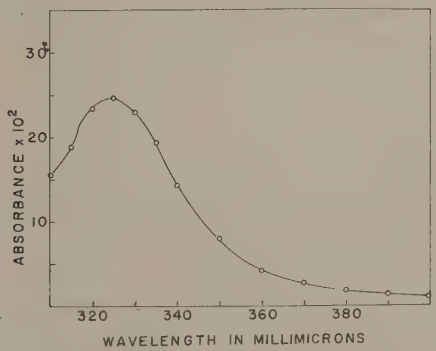

Fig. 1. Absorption spectrum of a solution 1.023×10^{-4} *M* in Nb and 4.0×10^{-3} *M* in PCA.

RESULTS AND DISCUSSION

In Fig. 1 the absorption curve for the niobium–protocatechuato complex in solution is shown. Maximum absorption occurs at 325 mμ. Keeping the Nb concentration constant and varying the concentration of the protocatechuate ion produced a

References p. 243

family of absorption curves all having the same absorption peak and general shape and not tending to cross each other. This suggested that only one absorbing species was present over the range of concentrations studied.

In Table I are given the absorption values at 325 mμ as taken from a typical series of curves.

TABLE I

ABSORPTION VALUES AT 325 mμ

Solution number	*Absorbance (A)*	*Total molar conc. of PCA* $\times 10^3$
1	0.1593	0.8
2	0.1911	1.6
3	0.2182	2.4
4	0.2328	3.2
5	0.2441	4.0
6	0.2534	4.8
7	0.2573	5.6

Total Nb concentration in each solution $= 1.023 \times 10^{-4}$ *M*.

When the absorbancy values, A, were plotted against the total molar concentration of the protocatechuate ion, C_{PCA}, curve number 1 of Fig. 2 was obtained. It was obvious that the absorbance had not leveled off and the complex was still considerably

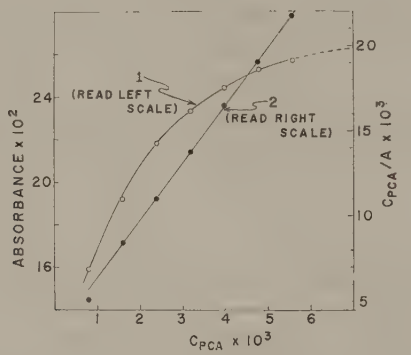

Fig. 2. Curve 1, absorbance as a function of PCA concentration. Curve 2, PCA concentration divided by absorbance as a function of PCA concentration.

dissociated, thereby prohibiting the evaluation of the limiting absorbancy, A_0 by graphical extrapolation. This difficulty was overcome by plotting instead (curve number 2 of Fig. 2) the C_{PCA}/A *vs.* C_{PCA} which produced a good straight line. The equation for this straight line is

$$C_{PCA}/A = (m)C_{PCA} + b,$$

where m is the slope and b the intercept. On rearranging this equation to give

$$A = \frac{1}{m + (b/C_{PCA})},$$

it becomes evident that A approaches the value of $1/m$ as C_{PCA} approaches infinity,

References p. 243

or the limiting absorbancy, A_0, equals $1/m$. By the method of least squares m was found to be 3.4264, consequently $A_0 = 0.2918$.

Let the formation of the complex species be represented by the following general equilibria:

$$MX_{n-m-p} + pX \rightleftharpoons MX_{n-m}$$

and

$$MX_{n-m} + mX \rightleftharpoons MX_n,$$

for which the formation constants would be

$$k_{n-m} = \frac{(C_{MX_{n-m}})}{(C_{MX_{n-m-p}})(C_X)^p}$$

and

$$k_n = \frac{(C_{MX_n})}{(C_{MX_{n-m}})(C_X)^m},$$

where n = maximum coordination number of the metal ion M, $X = C_{PCA}$, while MX_{n-m-p} and MX_{n-m} may be a hydrated niobium ion or a lower complex species.

Making use of the following variation of equation C 13 of NEWMAN AND HUME[11] (Note: the term M_t/M_0 in their equation is unity here since the Nb concentration was maintained constant in all solutions):

$$\log (A_0 - A)/A = -(m) \log C_{PCA} - \log k_n,$$

which holds true only if two species with one absorbing are present in solution, with the values quoted in Table I, it was found (Fig. 3) that a plot of $\log (A_0 - A)/A$ *vs.* $\log C_{PCA}$ produced a good straight line with a slope, $-m$, equal to 1 (actually 0.9635) and $k_n = 1.05 \times 10^3$.

Further verification that only one of the two species present was absorbing was obtained when the same data were substituted into equation C 12 of NEWMAN AND HUME[11] and a straight line (Fig. 4) resulted with an intercept of zero. This intercept,

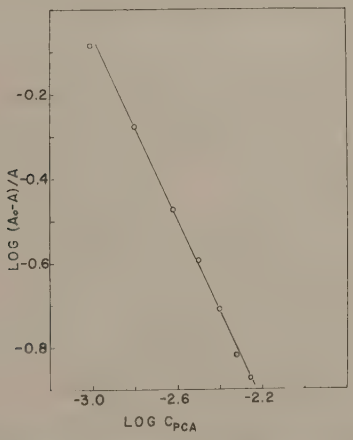

Fig. 3. Determination of the formation constant, k_n, with two species present and one absorbing.

References p. 243

which is the product of the molar concentration of Nb and the molar extinction coefficient of the MX_{n-m} species, could only be zero if the molar extinction coefficient were zero.

So far the results indicate only that one ligand was entering in the last step of the complex formation. However, with an indication that just two species are present,

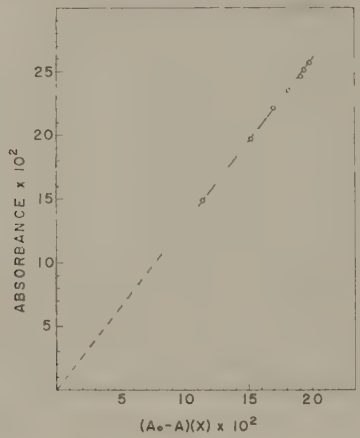

Fig. 4. Determination of the molar extinction coefficient of the second species with two species present. (Note: The absorbance values employed in this plot were calculated from the equation

$$A = \frac{1}{3.4264 + (0.002634/C_{PCA})},$$

for the best smooth curve (number 1, Fig. 2) of A as a function of C_{PCA}.)

one of which absorbs, it would appear that the MX_{n-m} group was a hydrated Nb ion or at least a species to which no PCA ligands were attached.

To rule out any possibility that the MX_{n-m} species might be a complex ion not absorbing at 325 mμ our data from Table I were substituted into equation C 11b of NEWMAN AND HUME[11],

$$[(A_0 - A)/A]X^m = [1/(k_n k_{n-m})][1/X^p] + 1/k_n,$$

which they have demonstrated to be obeyed by three species with one absorbing. A plot of $[(A_0 - A)/A]X$ *vs.* $1/X^p$, with $p = 1$, for our data gave a straight line of zero slope, thereby indicating that k_{n-m} must equal infinity, since k_n was known to be 1.05×10^3 from previous calculations. Such could only be true if the term $C_{MX_{n-m-p}}$ equals zero in the equilibrium constant equation for k_{n-m}. A third species, MX_{n-m-p}, was not present so the two species indicated were taken to be a hydrated Nb ion and the complex group MX_n. (Note: the PCA ion would not be considered since its effect was counterbalanced by the blank solution containing an identical PCA concentration used in the double beam spectrophotometer.)

These results indicated that $m = 1$ and the MX_{n-m} species contained no X group, *i.e.*, $n - m = 0$, so the equilibrium which existed was

$$M + mX = MX_n,$$

or the complex group present contained just one PCA group per Nb.

References p. 243

The relative order of stability of the three *ortho*-dihydroxy compounds studied thus far is protocatechuic acid, $k_1 = 1050 >$ pyrogallol, $k_1 = 840$[4] $>$ catechol, $k_1 = 540$[3], which is also the order of the observed[13] and expected acid strengths of the ligands. Whether this indicates that the formation of niobium complexes involves prior removal of hydroxyl groups from the hydrated niobium ion is uncertain. The available data point to such a mechanism, but more information about the nature of hydrated niobium species and the mechanisms of complex formation with niobium must be collected before this idea is proven.

By reacting a strong ammoniacal solution of protocatechuic acid with freshly precipitated hydrous niobium pentoxide, it was possible to isolate a solid complex compound which is believed to be $(NH_4)_4H_2[NbO(PCA)_3]\cdot 4H_2O$. It should be noted that the formula $(NH_4)_4[Nb(PCA)_3]\cdot 5H_2O$ would have the same percentage composition as the former. Efforts to establish conclusively the presence or absence of the niobyl structure by infrared analysis were unsuccessful; however, on the basis of previous experience the first-named formula is favored.

The red isolated compound was found to be very soluble in water, forming a clear, yellow solution, whereas it failed to dissolve to any extent in acetone, ethanol, chloroform, benzene or diethyl ether.

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BOOK REVIEW

Technology of Columbium (Niobium). Edited by B. W. GONSER AND E. M. SHERWOOD; New York, J. Wiley & Sons; London, Chapman and Hall; 120 pages; price 56 sh.

The rapid strides made in recent years in the use of high temperatures has led to a growing importance of the less common metals. Among these, element 41, known variously as Columbium, the name given to it by its discoverer CHARLES HATCHETT, and as Niobium, is outstanding. Although used hitherto almost exclusively as a ferroalloy, the pure metal also has great potentialities. It possesses a unique ductility and cold workability for a metal with such a high melting point (2468°C) though up to 1957 only a few tons had been produced. Its use in non-ferrous alloys however, has been steadily growing in importance.

Recognising the importance and potentialities of Columbium, a symposium was arranged by the Electrothermics and Metallurgy Division of the American Electrochemical Society in 1958 to cover a review of properties, the supply situation, extractive process metallurgy, analysis, effect of gases, alloy studies and related subjects. This book, under the general editorship of B. W. GONSER AND E. M. SHERWOOD, contains most of the papers presented at that time. The seventeen papers written by experts in the several fields secure a fairly complete coverage and point the way to future developments in the use of this important metal.

F. F.

CONTENTS

Beitrag zur Entwicklung warmfester Titanlegierungen
von U. Zwicker (Frankfurt/M.) 165

The availability, recovery and properties of rhenium metal
by I. E. Campbell, D. M. Rosenbaum and B. W. Gonser (Weirton, W. Va. and Columbus, Ohio) 185

Equilibrium diagrams with InSb as one component
by J. C. Woolley and D. G. Lees (Nottingham) 192

Equilibrium diagram of the Ga_2Te_3 – In_2Te_3 system
by J. C. Woolley, D. G. Lees and B. A. Smith (Nottingham) 199

A study of rhodium(III) perchlorate by paper electrophoresis and spectrophotometry
by S. K. Shukla and M. Lederer (Paris) 202

The oxytrichlorides and oxytribromides of niobium (columbium)(V) and tantalum(V)
by F. Fairbrother, A. H. Cowley and N. Scott (Manchester) 206

The uranium monocarbide–uranium mononitride system
by J. Williams and R. A. J. Sambell (Harwell) 217

Kinetics of the oxidation of uranium by carbon dioxide
by J. E. Antill and K. A. Peakall (Harwell) 227

Properties of titanium–aluminium–niobium alloys
by J. Suiter (Melbourne) 232

A spectrophotometric investigation of the niobium protocatechuic acid complex
by S. A. Brown and J. E. Land (Auburn, Ala.) 237

Book review 244

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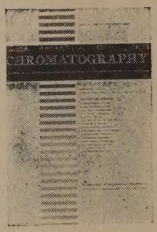

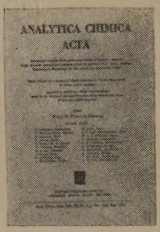

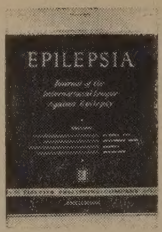

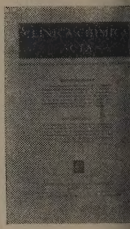

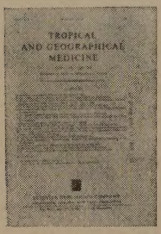

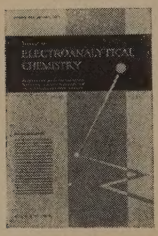

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